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ABSTRACT OF DISSERTATION

Aaron Robert Hutchison

The Graduate School

University of Kentucky

2007

THE DESIGN AND SYNTHESIS OF NOVEL CHELATES FOR THE PRECIPITATION OF MERCURY

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in the
College of Arts and Sciences
at the University of Kentucky

By

Aaron Robert Hutchison

Lexington, Kentucky

Director: Dr. David Atwood, Associate Professor of Chemistry

Lexington, Kentucky

2007

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ABSTRACT OF DISSERTATION

THE DESIGN AND SYNTHESIS OF NOVEL CHELATES FOR THE PRECIPITATION OF MERCURY

Mercury has been an element of great industrial importance since early times. This wide utilization of the element has led to pervasive mercury contamination in the global environment. Due to mercury's high toxicity, this is a matter of great concern. A number of methods, including phytoremediation, filtration, and precipitation/chelation, have been investigated to remove mercury from the environment. Unfortunately, these methods are not entirely satisfactory for the *in-situ* remediation of mercury from aqueous environments.

The hypothesis of this dissertation is that this can best be accomplished by the addition of a large and flexible sulfur-based chelate, that will bind mercury in a tetracoordinate and presumably tetrahedral environment, to mercury-contaminated waters. Although this proved difficult due to the tendency of these ligands to decompose into smaller, sulfur-containing rings, the synthesis and characterization of such a chelate was achieved. Several potential mercury-binding ligands were eventually synthesized significant amounts of mercury (91-100%) from the contaminated solutions, in one case lowering the mercury levels in the water to below the CVAF detection limits. The resulting solids lost little (<15 ppb) of their mercury during leaching studies.

This work demonstrates the use of tetradentate chelates in precipating Hg^{2+} from water to produce stable mercury-ligand precipitates. A calculation for the quantification of the geometry of a four-coordinate compound was also developed and applied to aluminum, gallium, and mercury compounds. This calculation could also be applied to the mercury compounds described in this thesis once X-ray structures become available

KEYWORDS: Mercury, Remediation, Thiols, Chelation, Precipitation

Aaron Hutchison

February 26, 2007

THE DESIGN AND SYNTHESIS OF NOVEL CHELATES FOR THE PRECIPITATION OF MERCURY

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February 26, 2007

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South Charleston, Ohio

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This work is dedicated to my parents and friends for all their support during my research.
It is also dedicated to God, from Whom all human originality and success originate.

ACKNOWLEDGEMENTS

The following dissertation, while representing my individual work, has been strengthened by the input of several individuals. First, I would like to thank my advisor, Dr. David Atwood, for his encouragement and support during my graduate career. I would also like to thank several other past and present members of the Atwood research group, including Dr. Sonali Bhandari, Dr. Burl Yearwood, Dr. Tim Keizer, Mr. Niladri Gupta, Mr. Taimur Shaikh, Mr. John Twyman, and Mr. Eduardo Santillion, for their advice and assistance during various stages of this work. Next, I would to thank my Dissertation Committee and outside examiner, Dr. John Selegue, Dr. Folami Ladipo, Dr. Robert Grossman, Dr. Chris Matocha, and Dr. Dibakar Bhattacharyya for their help at every stage of this process.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FILES

Chapter One: Mercury Pollution and Remediation

1.1 Mercury

Mercury is an unusual element, noteworthy both for its liquid state (m.p. –38.9°C) and high vapor pressure at room temperature (1.9 x 10^{-3} torr).[1] It also has the property of dissolving some metals to form amalgams. Due to this property, mercury is believed to have been used to extract gold, silver, and other metals from ore through amalgamation since as early as 2700 BC,[2] a practice that continues into the present. In nature, mercury is most often found as the reddish mineral cinnabar (HgS). Large deposits of cinnabar have been located and mined in Spain, the former Soviet Union, Yugoslavia, Mexico, Italy, North Africa, and California, with by far the largest deposit being at Almaden, Spain. Elemental mercury can be easily isolated from cinnabar by roasting. [1]

Mercury has an electron configuration of $[Xe]4f^{14}5d^{10}6s^2$. It is unique in that it is the only element outside of the noble gases to give off a monatomic vapor. It also has a high electrical resistivity. [1] Some of its unusual properties are due to the high relativistic effects experienced for mercury; the speed of its 1s electrons is greater than half the speed of light, leading to a contraction of the s and p orbitals and, due to greater shielding by the contracted orbitals, an expansion of the d and f orbitals.[3] This results in a net contraction of the overall atom and is largely responsible for the greater electronegativity seen in such large elements. Mercury exists in three forms, elemental Hg^0, monovalent Hg^I-Hg^I (Hg_2^{II}), and divalent Hg^{II}. Of these, it is interesting to note that the monovalent oxidation state is only found as bimetallic Hg^I-Hg^I, never as the monatomic Hg^I ion. Furthermore, this oxidation state is significantly less common than the elemental and divalent states. Mercury also shows a distinct tendency to form strong bonds with sulfur, to the extent that thiol compounds are sometimes known as mercaptans, from the Latin *mercurium captans* "mercury seizing".[4] This can at least partially be explained by the hard soft acid base (HSAB) concept. Sulfur is a quintessential soft base and Hg^{II} is one of the best examples of a soft acid. It has even been argued that the methylmercury ion serves as the "soft" equivalent of the "hard" proton.[5] Therefore, it is expected that combinations of mercury and sulfur-containing species would form stable compounds. Due to its soft nature, mercury is usually considered to more readily form covalent bonds with ligands than many metals.[1]

Mercury has long fascinated chemists due to its unusual properties. Mercury and sulfur (another element central to this study, which will be discussed in greater length later) were key reagents for the early alchemists and were utilized in pursuit of the transmutation of base materials to gold as early as 100 AD. In ancient China, mercury was used medicinally to kill lice and fleas. It was also given to patients in supposedly health-promoting elixirs, a practice which led to the death of at least three Chinese emperors.[6] Even though the emperors died, the Chinese alchemists considered the experiments at least partial successes, since decomposition was delayed in these victims. In reality, the highly toxic mercury compounds had killed all the microbial organisms in the body, along with the patient, thus delaying the onset of decay. The early European doctor Paracelsus used mercury to treat syphilis, a dubious practice that was continued until the twentieth century.[6] More positively, Lavoisier utilized mercuric oxide as his oxygen source during his groundbreaking study of the element.[7]

Mercury has remained an element of interest for chemists on into modern times. In the mid-1990's, a pair of structural reviews were published covering the coordination[8] and organometallic compounds[9] of mercury. Virtually all of the compounds found in both studies involved the divalent oxidation state. Among the coordination compounds, the most common coordination number was four and the most common geometry tetrahedral, with varying degrees of distortion. This was usually achieved by using four monodentate ligands or two bidentate ligands, rather than a single tetradentate ligand such as is the focus of the present study. For the organomercury compounds, however, a two-coordinate linear arrangement was overwhelmingly the most commom motif. One could therefore postulate that mercury coordination compounds have a marked preference for a tetrahedral geometry while the organomercury species prefer a linear geometry.

Tetrahedral geometries are almost always found for four-coordinate mercury. In the review of 125 four-coordinate mercury structures,[8] only once was a square planar geometry seen. This anomalous structure occurred when mercury was bound to the crown thioether 16S4 (figure 1.1a**)**.[10] The 16S4 was designed as a potential agent for mercury sequestration. However, the authors of the study came to the conclusion that a crown thioether was a poor choice, due to the much lower stability of the macrocyclic mercury complexes compared to their straight chain counterparts. This conclusion was supported by an earlier study, which had found that the formation constant for a 14S4 (Figure1.1b) mercury complex was 180 times lower than that for its straight-chain counterpart (Figure 1.1c).[11] This effect can be partially ascribed to the tendency of the C-S bonds in crown thioethers to adopt a gauche conformation, which results in structures that do not favor chelation.[12] However, this alone cannot fully explain mercury's less strong binding to macrocycles, for the macrocyclic effect is also not evident when crown amines bind mercury.[13] It appears that mercury would prefer to be in a tetrahedral geometry, rather than the square planar geometry enforced by a macrocycle, a situation that is known to be common for d^0, d^1, d^2, d^5, and other d^{10} metals as well.[14] For a d^{10} metal such as mercury, this can be being placed in an antibonding orbital.[3] Studies have also shown that a thiocrown ether must have at least 16 members to successfully encircle a Hg^{II} ion; anything less and the cavity will be too small.[15] In the context of designing a more effective mercury binding agent, this suggests

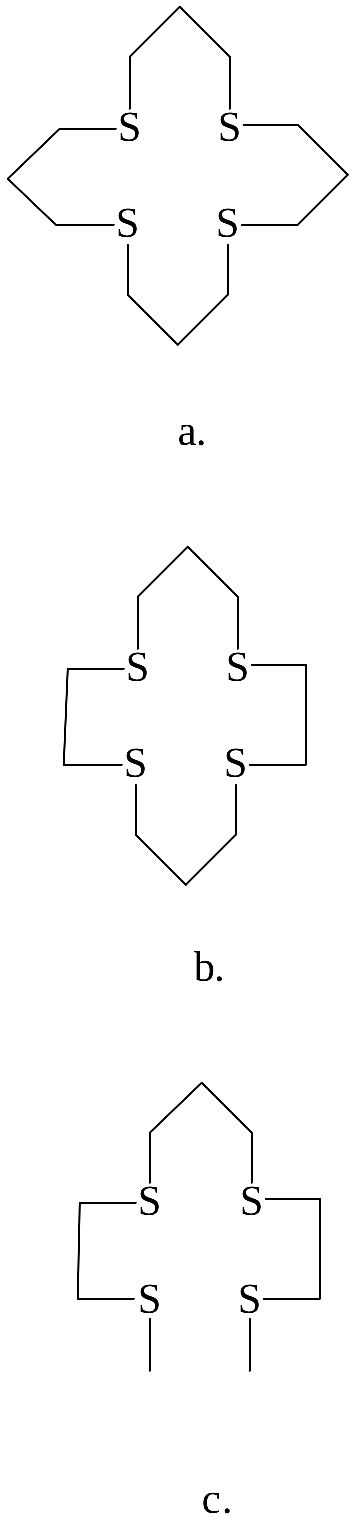


Figure 1.1: Thioethers

that at least three carbons should separate each sulfur in a single ligand having four mercury binding sites.

1.2 Methylmercury and Human Mercury Poisoning

The ubiquitous bioinorganic cofactor cobalamin has been called "nature's most beautiful cofactor",[16] but it is also perhaps one of nature's most deadly. It is one of the forms of vitamin B_{12} found in humans and is responsible for methyl transfer reactions.[17,18] Methylcobalamin contains a cobalt (III) atom in an octahedral geometry, with four nitrogens equatorial, a methyl axial, and a fifth, pendant nitrogen also axial (figure 1.2). In sulfate-reducing bacteria such as *Desulfovibrio desulfricans,* methylcobalamin can methylate inorganic Hg^{II} through an enzymatically catalyzed reaction.[19] The mechanism of this reaction is not fully understood, although it is believed to be a one-step process in which the mercury does not bind to the cobalt.[20] The resulting methylmercury is stable even in water, due to the more covalent nature of the mercury-carbon bond and the kinetic stability of methylmercury to hydrolysis.[21]
Although toxic to humans in all its forms, the methylated form of mercury is by far the most toxic, with only a few drops of dimethylmercury on the skin proving lethal.[22] This is not due to any change in the mercury's inherent reactivity after methylation, but rather due to a dramatic increase in the absorption of the lipophillic methylmercury by the body and an increased likelihood of retention rather than excretion.[23] The liver reabsorbs, rather than excretes, methylmercury, leading to its bioaccumulation in the food chain. Methylmercury also crosses the blood-brain barrier and tends to accumulate in the brains[23, 24] of mammals (and in the muscles of fish),[23] while inorganic mercury to a lesser extent will accumulate in the human kidney.[25]

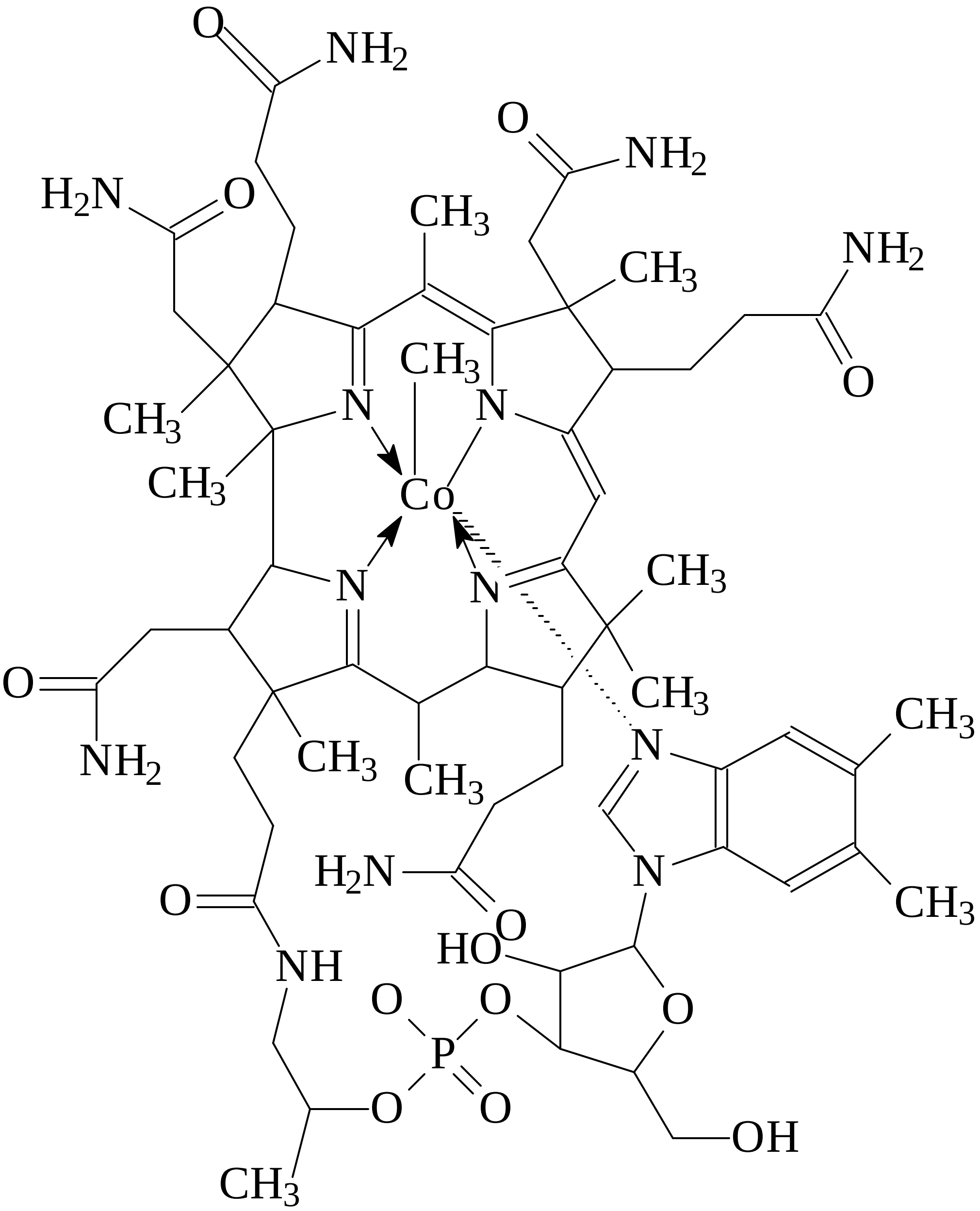


Figure 1.2: Methylcobalamin

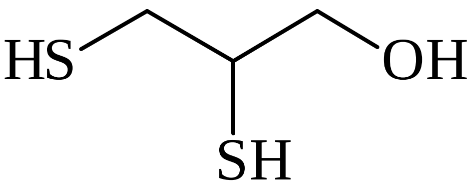
Once inside a human, mercury can cause a number of serious health problems. It is probably best known for attacking the central nervous system, an assault which on a chemical level is believed to primarily involve mercury binding to key biological sulfur residues,[26, 27] although it can also trigger a dramatic influx of Ca^{2+} across cellular membranes,[28] generate reactive oxygen species,[28] and trigger an autoimmune response.[27,29] The autoimmune effects of mercury are particularly interesting and require further study; it is currently believed that this is the mechanism by which mercury attacks the kidneys,[27] and there is significant evidence that mercury exposure can trigger systemic lupus erythematosus, an autoimmune disease commonly known as lupus.[30] Mercury can also cause a general impairment of the immune system, especially if the exposure occurs prior to or just after birth,[31] leaving the victim vulnerable to attack by other pathogens.[27] There also is evidence for a correlation between methylmercury exposure and heart disease.[32] All forms of mercury, including elemental mercury such as is released by dental amalgams (see section 1.3), are also known to accumulate in the placenta of pregnant women and inhibit the development of the fetus.[30, 33]

The symptoms of serious mercury poisoning in adults include irritability, upset stomach, either pain or a loss of feeling in the hands and feet, constriction in vision, tremors, loss of hearing, and eventually death.[30, 34-37] Interestingly, for dimethylmercury, symptoms usually do not appear until several months after exposure. This is apparently linked to the fact that the attack of a thiol on dimethylmercury, while thermodynamically favored, is kinetically slow.[38] Methylmercury is also known to be highly damaging to prenatal brain development, with children exposed before birth often showing retardation, cerebral palsy, and premature death.[30] Although much of the world's current concern over methylmercury poisoning has therefore been focused on preventing prenatal exposure, recent studies suggest that adults begin to suffer damage to the central nervous system, resulting in reduced fine motor skills, tremors, attention span, and memory loss, after exposure to much lower levels of methylmercury than previously suspected.[29, 32]

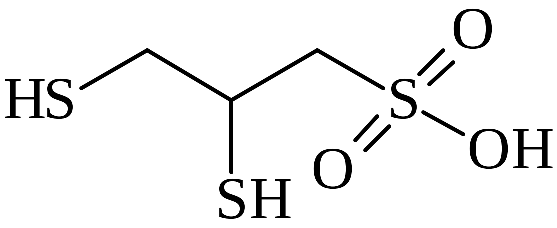
History records several major cases of methylmercury poisoning. When methylmercury was first successfully synthesized and reported in the late 1850's, two of the chemists working on the project died and a third was debilitated.[36] In 1956 residents of the Minamata Bay, Japan area began coming down with a strange nervous disorder. This was eventually diagnosed as methylmercury poisoning due to waste dumped by the Chisso Minamata acetaldehyde plant (mercury sulfate is a catalyst for the synthesis of acetaldehyde[39]) and the Minamata Chemical Industrial Plant and Company into the bay. By 1998, 2,262 residents of the region had been diagnosed as suffering from the poisoning and 1,289 have now died,[40] although it is very debatable whether all those deaths can be blamed on mercury. Due to this incident, methylmercury poisoning is now known as Minamata Disease. In September 1971, due to fears of famine, Iraq imported large amounts of seed wheat, which had been treated with methylmercury fungicides, a common practice at that time. Unfortunately, a great many Iraqi farmers apparently subscribed to the theory that a grain in the oven was superior to a stalk in the field and consequently converted the wheat into flour for making bread, rather than planting it. By January 1972, hundreds of cases of Minamata Disease were being reported in Iraq each day. By February of that year, when the epidemic appeared to have ended, at least 6,530 people had been hospitalized and 459 had died, making this the largest case of mercury poisoning ever recorded.[34] Currently a new epidemic of Minamata Disease is building in the Amazon River region, where gold mining has resulted in widespread mercury release into the river. This problem has been compounded by the presence of hydroelectric reservoirs in the region, which create anoxic regions ideal for mercury methylation.[41] As a result, methylmercury is bioaccumulating in the region's fish. Although no deaths have yet been reported, as much as

78% of the population of some fishing villages now show elevated mercury levels and many people appear to be suffering from mild cases of Minamata Disease.[2, 29, 35, 42]

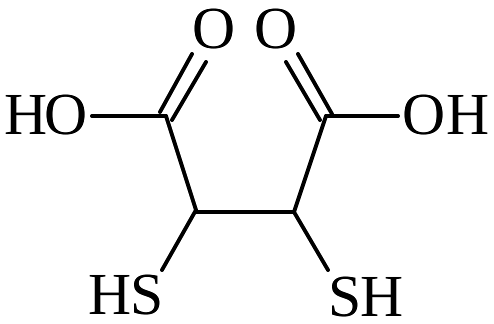
Inorganic mercury poisoning is usually treated by chelation therapy. In this process the patient is given some chemical compound that will potentially chelate the mercury, with the resulting complex being more easily excreted than the original mercury in the person's system. Traditionally, dimercaprol, also known as British anti-lewisite (figure 1.3a) and originally developed as a treatment for arsenic-based chemical weapons attack, was the preferred chelate for this treatment.[43] However, dimercaprol is not very water soluble, must be given through an intramuscular injection (requiring that the patient remain hospitalized during the course of treatment) and the resulting mercury complex may accumulate in the brain prior to excretion, causing the very damage it was supposed to prevent.[44] Much preferred today is 2,3-dimercapto-1-propane sulfonic acid (DMPS, figure 1.3b), usually administered as its mono-sodium salt.[25, 43, 44] It has been reported that DMPS can remove up to 1 mg of mercury a day from the body[26] and it can potentially prevent the kidney damage often associated with inorganic mercury poisoning.[25, 26] In cases of extremely heavy inorganic mercury poisoning, dialysis in conjunction with DMPS treatment can also prevent permanent damage.[43] DMPS and the somewhat similar ligand *meso*-2,3-dimercaptosuccinic acid (DMSA, figure 1.3c) have also been reported to inhibit the teratogenic effect of methylmercury in mice.[33, 45] However, there are some dangers in using chelates such as DMPS and DMSA. Both can bind biologically essential metals such as zinc and remove them along with the mercury, and recent studies suggest that both may also have an inhibitory affect on some human enzymes, so clearly there is room for more research in this field.[46]



a. British anti-lewisite



b. DMPS



c. DMSA

Figure 1.3: Chelation therapy ligands

1.3 Industrial Uses of Mercury

An important and often overlooked industrial use of mercury is in the lighting industry. Most fluorescent lamps utilize mercury vapor, along with an inert gas such as argon, to convert electrical discharge to useful light.[47, 48] Due to the rise in regulations for the disposal of mercury-containing waste, the industry is currently seeking ways to decrease the mercury content of these lights.[49] However, it is ironic that the current generation of "environmentally friendly" compact fluorescent bulbs do contain mercury, although the energy saved by their use does appear to outweigh the disposal issues associated with them.

Another major industrial use of mercury is in electrolytic cells used in the chloralkali industry. Chloralkali plants produce sodium hydroxide and chlorine gas through the electrolysis of brine. In this process mercury serves as the cathode, converting the sodium cations to sodium metal, amalgamating the sodium, and carrying it into a second reaction vessel, where it reacts with purified water to form sodium hydroxide.[50] Although this is theoretically a sealed system where the mercury is recycled, in practice it can be a significant source of industrial mercury pollution.[51, 52] Due to this, mercury cells are currently being replaced by more modern mercury-free diaphragm cells.

Mercury cell batteries were also once widely used for applications such as hearing aids, but they are now being phased out. The standard mercury cell battery contains a mercury/zinc amalgam as the anode and a mercuric oxide/graphite cathode. Mercury is also found in zinc-silver cell batteries (such as sometimes used in watches), where a mercury/zinc amalgam again forms the anode. Traces of mercuric chloride are occasionally found in zinc-carbon batteries.[53, 54]

The high toxicity of mercury has also been exploited for several industrial applications. For example, organomercurials have been widely used as pesticides[55] or as fungicides for the treatment of seeds. They have also been added to paints as fungicides[56] and pharmaceuticals as an antimicrobial and/or antibacterial agent.[57] Thimerosal (sodium ethylmercurythiosalicylate) is the most widely used preservative for contact lens solutions and vaccines.[58]

For well over a century, mercury has been combined with silver, copper, and other metals to form dental amalgams. These can contain as much as 50% mercury. Until very recently these were by far the most the most common tooth fillings; by 1995 up to 100,000 kg of Hg^0 a year was used for fillings, and they remain popular today among dentists.[59] Although dental amalgams are not considered a major source of environmental mercury pollution, they are a potential source of exposure to individuals. Studies have uncovered evidence of increased mercury levels[44] and mercury poisoning among dentists.[36] Furthermore, there is a growing debate about the exposure of patients with amalgams. There is significant evidence that people with large numbers of amalgam fillings have higher levels of mercury in their bodies than those without,[60, 61] and there is anecdotal evidence of dramatic health improvement in some patients suffering from chronic fatigue syndrome and "flu-like" illnesses after amalgam removal.[62] Furthermore, work by Dr. Boyd Haley and other have pointed to a possible link between dental amalgams and Alzheimer's disease and other brain disorders.[59, 63, 64] It is interesting to note that, while Alzheimers has never been linked directly to Minamata Disease, there are several shared neurological symptoms, and both illnesses do involve severe neurological damage.[28] The differences could arise from the slightly different reactivity in the body between mercury vapor (Hg^0) and methylmercury (Hg^{II}). There is also evidence that amalgam fillings can lead to oral lesions in some patients.[65]

1.4 Environmental Mercury Pollution

As an element with a high vapor pressure, mercury is present in the atmosphere with its own environmental cycle (figure 1.4). Mercury vapor (Hg^0) can be introduced into the atmosphere through many routes, including volcanic activity,[66] mineral deposit degassing in the Earth's crust,[67] emission from vegetation[68] (especially during forest fires[69]), and leaching from sediments as Hg^{II},[70] which can be reduced to Hg^0 and evaporate.[21] Mercury vapor is then oxidized in the atmosphere to Hg^{II} and deposited back in the environment primarily by precipitation. There it can be reduced again to continue the cycle.[21] Studies of core samples from lake bottoms,[71] glacial ice cores,[66] and peat bogs[71] show a steady background of mercury deposition for centuries. A particularly clear study was performed using ice cores from the upper Fremont glacier in Wyoming, which showed mercury deposition from the atmosphere between roughly 1720 and 1993 (figure 1.5).[66] Prior to the industrial age, the ice cores showed an average background mercury concentration of around 3 ppb. These values spiked to approximately 15 ppb at a core depth coinciding with the 1815 eruption of Tambora. Similar spikes, to even higher concentrations due to the increased background from the start of the industrial age, can be seen for the eruptions of Krakatau and Mount St. Helens. Around 1850, the mercury level in the core rises dramatically to around 17 ppb, coinciding with the start of the western gold rush. There is a noticeable drop corresponding to the US Civil War. After the war, the level rises again until dropping off in the early 1880's, when the use of mercury in western gold mining was historically recorded to have declined. It soon rises again, with an increase to ~ 7 ppb from the rise in manufacturing during WWI, a drop off during the Great Depression, and another rise (to around 10 ppb) coinciding with the second world war. From there the mercury concentration steadily rises, peaking around 25 ppb between the late 1980's and early 1990's. During the 90's, the mercury concentration decreases, dropping to closer to 16 ppb as new regulations on mercury pollution take effect. The ice core data suggests that as much as 70% of the mercury deposited in the last 100 years came from anthropogenic sources. These finding are in accord with studies conducted on lake sediments and peat bogs.[71,72]

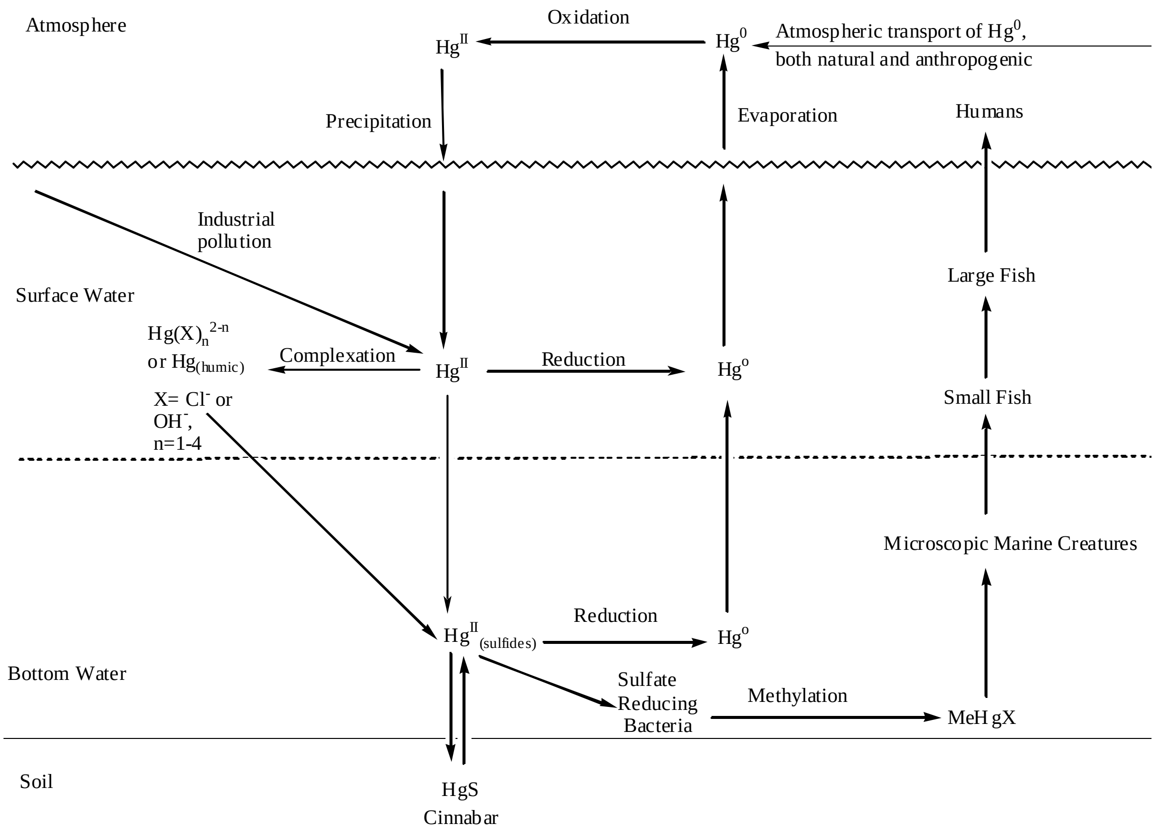


Figure 1.4: The geochemical mercury cycle

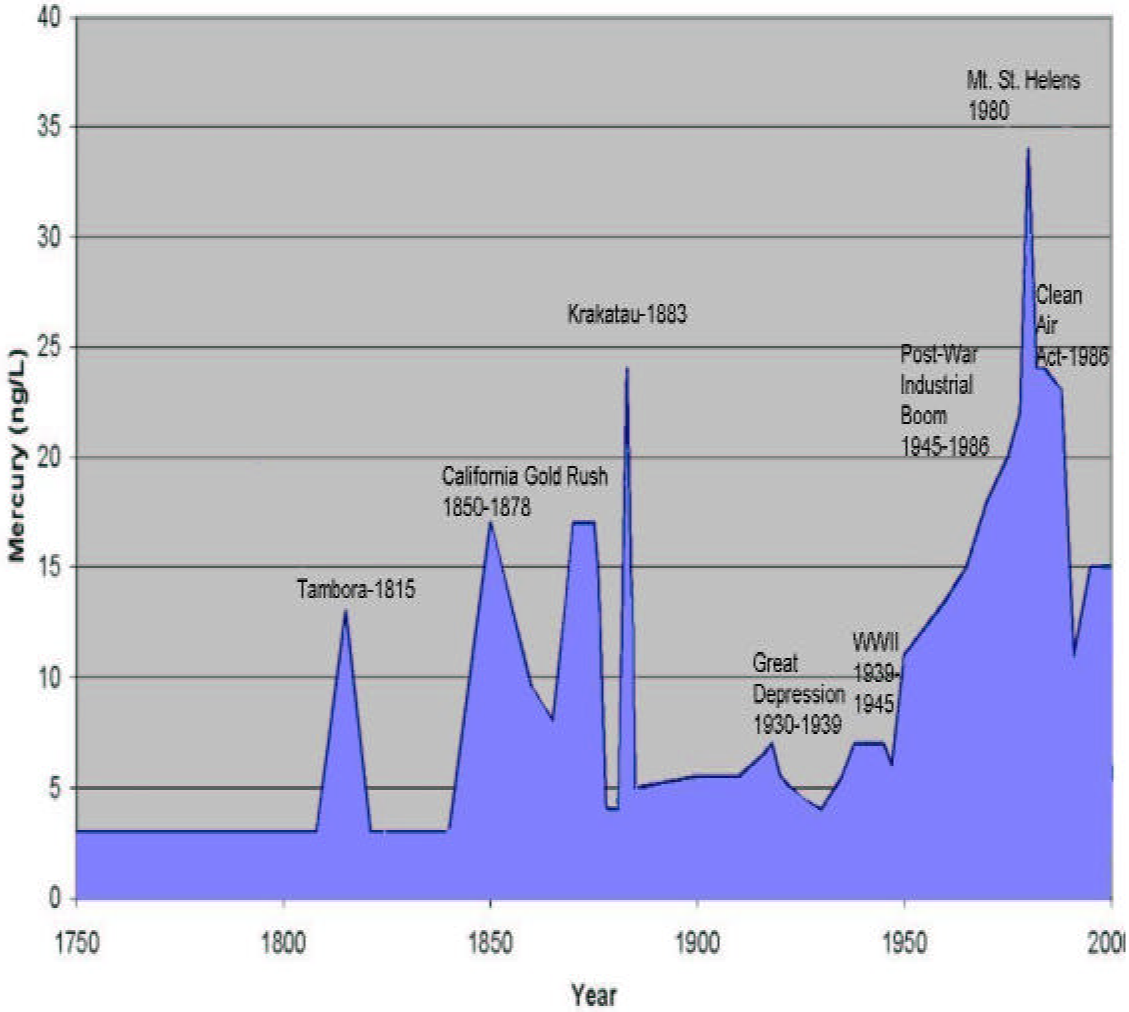


Figure 1.5 Mercury deposition as recorded by the Upper Fremont Glacier since 1750 (based on data from Schuster, P. F.; Krabbenhoft, D. P.; Naftz, D. L.; Cecil, L. D.; Olson, M. L.; Dewild, J. F.; Susong, D. D.; Green, J. R.; Aboot, M. L. *Environ. Sci. Technol.* **2002**, *36*, 2303.)

Approximately 50% of the mercury entering the atmosphere each year comes from new anthropogenic sources. Many of the natural sources are simply recycling mercury deposited earlier by human activity, however, so the actual percentage of the environmental mercury load due to anthropogenic sources is greater than 50%.[73] Anthropogenic mercury pollution originates from several sources. For over 300 years, Spanish gold and silver mining in South America resulted in an estimated 216,000 tons of mercury being deposited in the environment.[2] Approximately 61,000-66,000 tons may have been released on the North American continent during the period of the gold rushes,[72] and current gold mining in the Amazon region is resulting in the release of as much as 165 tons a year.[2, 41] Illegal gold mining has recently led to mercury pollution in Indonesia's Minahasa Penninsula.[74] Also, mercury is sometimes released during the smelting of metals, including copper and zinc.[75]

Another source of potential mercury pollution is fossil fuels such as coal. This issue is the subject of a recent literature review.[76] Coal contains variable amounts of mercury compounds (averages from 0.87-0.01 µg mercury per g coal), with Gulf Coast lignites and Appalachian bituminous coal having the highest concentrations found in the United States.[77, 78] Although the concentration of mercury released is small (0.001-0.003 ppb),[48] the total amount released can be quite significant, due to the enormous quantities of coal that are consumed worldwide. In fact, the US EPA considers this to be the largest single source of atmospheric mercury emissions in the United States today, releasing an estimated 42-48 tons a year.[76, 79] Although coal is considered the worst energy source for mercury pollution, some can be found in petrochemicals such as oil as well.[56] Elemental mercury vapor (along with gaseous or particulate inorganic mercury and organomercury compounds) is also often associated with natural gas. This can lead to elevated mercury levels in the soil (up to 40 mg/kg) and water (up to 3 g/L) near gas processing plants and, because this includes metallic mercury vapor that is fully capable of amalgamating many metals, serious corrosion of on-site equipment. Another combustion-based source of mercury pollution is waste incineration, which may account for as much as 40% of the mercury emitted in North America.[73] The mercury source here is primarily discarded fluorescent lamps and batteries. A study has suggested that this was the primary source of atmospheric mercury release for maritime Canada in the mid 1990's, although it was expected to be overtaken by fossil fuel burning in the future as mercury-based batteries are phased out.[73] Due to a greater use of thermometers and batteries among health care providers, medical waste tends to be particularly high in mercury and is viewed as a continuing problem by the US EPA.[80] Another related source is crematoria, where mercury is primarily released from dental amalgams in a cadaver's teeth. Although the amount released is fairly small (kg/year level), it is a significant portion of the total mercury released from some nations, such as Sweden.[81] Furthermore, elevated mercury levels have been found in soil downwind of crematoria[82] and in the hair of crematoria employees.[83]

The release of mercury into water, although believed to occur in much smaller amounts than release into the atmosphere, is a matter of at least as great a concern and has been recently reviewed.[84] History's most famous case of mercury poisoning, resulting from the dumping of mercury contaminated waste into Minamata bay, Japan,[85] has already been discussed in detail. Aqueous anthropogenic mercury pollution tends to occur due to mercury-contaminated waste streams draining into bodies of water. For example, not only can mercury evaporate from landfills or precious metal mining operations, it can also leach into nearby waters. Furthermore, abandoned gold, silver, or mercury mines can be areas of particular concern. A number of such mines are located in the American west, and studies there have found significant mercury levels in nearby soil and water.[86]

1.5 Mercury Geochemistry

It is estimated that between 6,000 and 10,800 tons of mercury reside in the atmosphere at any given time.[87] Although most mercury enters the atmosphere as Hg^0, a significant amount also resides there as Hg^{II} in atmospheric water droplets. It is estimated that mercury vapor (Hg^0) has an atmospheric retention time of around one year. During that period it can travel a considerable distance, resulting in elevated mercury levels far from the originating source. Atmospheric mercury chemistry is a significant area of research, with several reviews published over the last few years.[87-89] This chemistry is dominated by a series of only partially understood redox reactions that occur in both the gaseous and aqueous phases. In water droplets, Hg^0 can be oxidized to Hg^{II} by ozone, reactive chlorine species (HOCl or ^{-}OCl), and to a lesser extent by hydroxyl radicals. Competing with this is the reduction of Hg^{II} to Hg^0, which can be accomplished by sulfite, provided that sulfite is present due to pollution. If sulfite is not available, the reduction can be accomplished at a slower rate by hydrogen peroxide radicals. Exactly which processes dominate is not known at this time, although it is assumed that overall oxidation occurs more rapidly than reduction, since the mercury does eventually tend to return to earth as Hg^{II}. Most of these redox reactions are believed to occur in the aqueous phase.[21] Gaseous Hg^0 can be oxidized to Hg^{II} by a number of molecules, including ozone and hydrogen peroxide during the day and nitrate radicals by night. It appears that sunlight increases the rate of mercury oxidation in the gas phase, although the reason for this is not known.[87] More research in this area is required before the atmospheric chemistry of mercury is fully understood.

The aqueous geochemistry of mercury is also an important field of research. This chemistry is dominated by the tendency of mercury to become bound to organic or sediment particles as well as by changes in its oxidation state and form (figure 1.5). An excellent review is available on the subject.[21] The speciation of mercury in water is in a large part dependent on its depth, with very different reactions occurring in higher, more oxygen-rich waters than in lower, oxygen-poor zones. In both layers, mercury is divided to a varying degree between forms bound to particulate matter and dissolved species. In the upper oxic layer, these dissolved species include $Hg^0_{(aq.)}$, Hg^{II}, and methylmercury, with Hg^{II} probably predominating. These do not exist as free divalent mercury ions, of course, but as various ligand mercury combinations with the general formula $Hg(X)_n^{2-n}$, where X is hydroxide or chloride and n ranges from one to four. Mercury sulfides can also be found, although not in as high a concentrations as associated with lower anoxic waters. Depending on the dissolved organic content of the lake and the abundance of reduced sulfur species in the organic material,[90] as much as 95% of a lake's Hg^{II} can also be bound to humic matter.[21] It has also been demonstrated that sufficient chloride concentrations to yield $HgCl_2$ but not significant amounts of $HgCl_3^-$ or $HgCl_4^{2-}$ will result in increased mercury uptake by bacteria and therefore potentially can lead to methylation in the locally anoxic bacterial biofilms that can exist even in these waters.[91]

It is possible for this Hg^{II} to be reduced back to Hg^0 through two routes, photoreduction or bacterial action, with the bacterial route predominating in high mercury waters. As this route is a key factor in some remediation schemes, it should be described in detail. Some bacteria contain a series of genes known as the *mer*-operon. The *mer*-operon directs the bacteria to produce an enzyme called merA, which converts divalent mercury to elemental mercury, which is then excreted as vapor. In the presence of methylmercury, a second enzyme, merB can also be created that catalyses the hydrolysis of methylmercury, prior to reduction by merA.[92, 93] There is some evidence to suggest that the presence of dissolved organic material can facilitate the oxidation of mercury. However, it has been shown that in high chloride waters, a significant percentage of Hg^0 can be photooxidized back to Hg^{II} before evaporating,[94] although direct photoxidation is less significant in freshwater.[95] Furthermore, photolysis of dissolved organic material can produce hydroxyl radicals, which are also capable of reoxidizing the mercury.[90] There is clearly room for more research on the redox chemistry of mercury in natural waters.

In many cases, especially in lakes or coastal areas with significant shore runoff, the highest concentrations of mercury are found in deeper, more anoxic waters.[7] The geochemistry of mercury in this region is significantly different from its chemistry in more oxygen-rich layers.[21] Virtually all of the mercury is bound to sulfide, many times with the formula $HgS_2H_m^{m-2}$ or as cinnabar. In the presence of elemental sulfur, mercury polysufides can also form. Although cinnabar itself is relatively insoluble, it can be converted to other, more soluble sulfide species, explaining the higher levels of dissolved mercury often found at these depths. Recent studies also suggest that cinnabar is more soluble in acidic solutions containing chloride ions[96] or waters high in thiol-containing organic matter[90] than previously believed. Although there are some reports of abiotic reduction of mercury by humic acid in this region, the primary reaction of interest is mercury methylation.[7, 21] A key question is how the mercury is absorbed by the bacteria to be methylated in the first place. Due to its more covalent bonding, $HgCl_2$ is reasonably soluble in lipids and can therefore be absorbed through the cell walls of unicellular organisms. But $HgCl_2$ is not a significant species in the anoxic depths. However, it has been theorized that $Hg(SH)_2$ or mercury polysulfides may possess similar solubility. If that is the case, these are probably the species methylated. This view is supported by recent studies demonstrating that mercury methylation rates are reduced when a large excess of Fe^{2+} is added to a system. It was postulated that this was due to the iron competing with the mercury for the available sulfur.[97] It is worth noting that the primary methylmercury species in these waters is CH_3HgS^- and its protonated counterpart. Due to its solubility in lipid membranes, methylmercury can be absorbed into unicellular organisms, which are in turn devoured by higher organisms. Once ingested, almost no higher organism excretes significant amounts of methylmercury. The result is that the compound accumulates in larger fish and can eventually be consumed by humans.[21]

Many areas of environmental interest do not involve a purely aquatic system as much as they do a land/water interface. The speciation of mercury in these “real world” situations can be complex. Therefore, it is best shown by summarizing mercury’s behavior in two environments; an abandoned mercury mine in the American west and the Everglades swamp in Florida.

Mercury mining became important in the American west because of the need for mercury to support the gold rush. At these mines, the cinnabar-containing ore was roasted to liberate the elemental mercury. The calcines (waste rock remaining from the roasting) were simply tossed aside at the mine location. Today water can seep out of the mine, run through the calcines, and enter nearby streams. A detailed study has been performed on the mercury chemistry and speciation during this process.[86] Initially, the mine drainage is weakly acidic and shows only a low to moderate concentration of mercury. However, the sulfate concentration is significantly elevated. As the water exits the mine, it flows through the calcines and waste rock, which normally contain a high content of soluble mercury. As a result, the mercury concentration of the water increases, often by orders of magnitude. Furthermore, the water retains its high sulfate content. This makes it the perfect medium for sulfate-reducing bacteria to methylate mercury. Much of the resulting methylmercury is adsorbed onto the surface of iron oxyhydroxide, which precipitates as the waters, also rich in iron, are exposed to atmospheric oxygen. However, enough methylmercury enters the streams to pose a serious problem. Dangerously elevated methylmercury levels have also been noted downstream in the Sacramento River Basin during periods of flooding, demonstrating the mobility of this contaminant.[70] Conversely, a study on mercury mines in Nevada, while finding elevated mercury levels in the calcines and the soil near them, did not find overly elevated levels in the local stream system, due to the geographical isolation of the mines from the streams.[98]

The problem of mercury in the Everglades is distinctly different from that in California, because there is no obvious source of the Florida pollution. Rather, the mercury appears to have been deposited naturally from the atmosphere. Once in the water, it is being retained and rapidly methylated.[99] As atmospheric mercury levels tripled due to pollution from the industrial age, more mercury was deposited in the Everglades, where it was methylated to a greater extent than in most areas. The result is a situation in which around 20% of the mercury in Everglades surface waters is methylmercury.[100] The waters of the Everglades contain very high concentrations of organic matter. About 10% of this is particulate mater, while 30%-60% is colloidal and the rest is truly dissolved. The majority of the inorganic mercury is associated with colloidal organic matter. On the other hand, the majority of the methylmercury is associated with the smaller particle size colloids or in the truly dissolved phase. In fact, the level of methylmercury is strongly correlated to the level of dissolved organic carbon. The dissolved organic carbon presumably serves as a feedstock for the methylating bacteria. Due to the high organic matter content of such a large swamp there is an excess of such bacteria and therefore an increased rate of mercury methylation and retention.

1.6 Mercury Analysis

Due to the metal's importance as a pollutant, the determination of mercury content in various environmental samples is an area of significant research. The mercury content of a sample is generally determined by spectrographic means, usually cold vapor atomic absorption spectroscopy (CVAAS) or cold vapor atomic fluorescence spectroscopy (CVAFS). A cold vapor technique is simply one in which the analyte is rendered volatile without significant heating. In the case of mercury, this simply means reducing all the metal in a sample to the volatile elemental form. In practice, this is accomplished by injecting the sample into a reaction vessel, then adding a chemical reductant.[101] The most commonly used reductants are $SnCl_2$[102] or $NaBH_4$,[103] with the tin reagent being more widely used, but sodium borohydride (sodium tetrahydridoborate) is growing in popularity.[101] When tin is used, an inert carrier gas, usually argon, is required to carry the vapor to an irradiation chamber, while with borohydride, hydrogen generated during the reaction can serve as the carrier gas.

Atomic absorption spectroscopy is a well-established analytical technique.[104] The basic principle behind this method is that many analytes absorb light at a characteristic wavelength. For mercury, this wavelength is 253.7 nm.[101] If the intensity of light passing through the sample is compared to the intensity of light (from the same source) passing through a blank, the difference indicates the light absorbed. This can be directly related to the concentration of analyte.[104] This method has a long history of use in the analysis of mercury vapor, having been first used for that purpose in 1939.[101] There is a significant limitation, however. In measuring absorbance, one is essentially measuring the relatively small difference in two relatively large quantities.[104]

To avoid this problem, the technique of atomic fluorescence spectroscopy was developed. The basic principle behind this method is similar to that for atomic absorption (and it is even possible for one instrument to provide both forms of analysis). Once again, the mercury is irradiated with 253.7 nm light and this light is absorbed by the mercury. The excited mercury atoms return to ground state by fluorescing and the fluorescence is measured by a detector placed at 90° to the light source. Therefore, the concentration of mercury is determined by direct comparison to the fluorescence of the sample, rather than looking at the change in the light's intensity as it passes through the sample. This allows for a greater sensitivity than atomic absorption techniques and hence slightly lower detection limits.[104, 105] The US EPA has endorsed CVAFS (when coupled with absorption/desorption techniques to be discussed shortly) as the preferred method of mercury analysis.[106]

Sample preparation is a major concern in the analysis of most environmental analytes, and mercury is no different in this regard. While it is possible to take a clean mercury solution created in the lab, treat it with some mercury remediation agent, filter, and directly anylze the filtrate for its remaining mercury concentration, this scenario cannot be applied to true environmental samples. Water, soil, and biological samples harvested in the field usually contain multiple forms of mercury and may contain other metals or organic compounds that could interfere with the spectroscopy. Therefore samples are usually digested prior to analysis. In standard acid digestion, a strong acid or combination of acids is added to the sample, along with an oxidizing agent such as potassium permanganate, hydrogen peroxide, or potassium dichromate. The mixture is then mildly heated (the temperature is usually kept below 100° C), in many cases for an extended length of time.[101] The heating in acid serves to decompose most solid matrices to which the mercury may be bound, while the oxidant converts any elemental mercury (Hg^0) to water soluble divalent mercury (Hg^{II}). At the end of the procedure (and just before the analysis of the sample) hydroxylamine hydrochloride or oxalic acid is usually added to the sample to eliminate any unreacted oxidant, thereby assuring that it will not interfere with the reductant added in the vapor generation chamber. Recently, microwave irradiation in a sealed vessel has been substituted for heating in an open vessel during digestion.[107-110] An alternative to standard acid digestion is pyrolysis, in which the sample is heated to approximately 800 °C and the resulting mercury vapor is captured on a gold surface for later desorption and analysis.[107]

Even when samples are digested using standard hot acid or microwave techniques, it is becoming increasingly common to trap the mercury on a gold surface (usually gold gauze) prior to analysis. This permits large amounts of mercury to be concentrated before analysis and thereby makes it possible to analyze more dilute samples.[101] This procedure is now widely considered the best method for the detection of ultratrace amounts of mercury in samples and is included in the US EPA's standard procedure for mercury analysis.[106]

Up to this point, the discussion has centered on simply determining the total concentration of mercury in a sample. However, mercury toxicity and behavior is largely dependent on its form; a high concentration of methylmercury is a matter of greater concern than the same concentration of elemental mercury. Therefore, it is crucial to determine the speciation of a sample's mercury. There are a number of ways of accomplishing this, with no one method appearing ideal for all samples.[101] A recent review has nicely summarized the techniques currently available for the speciation of environmental mercury samples.[111] Often it is considered sufficient to simply separate the inorganic mercury salts from the organomercury compounds. This is usually done by assuming that inorganic mercury is more easily reduced than organic mercury.[110] The sample is extracted (usually with dilute HCl) rather than digested and analyzed by normal CVAFS. Then a second aliquot of sample is fully digested, with an oxidizing agent and strong acid, and also analyzed. The difference between the resulting mercury concentrations is considered to be the total organic mercury concentration. Alternately the organomercury compounds can be extracted from the inorganic mercury, often by alkaline rather than acidic digestion,[111] and then each layer analyzed separately by CVAFS[112, 113] or both can be trapped on a thiol impregnated silica column then separately eluted and analyzed.[114] If more detailed information is required, it is possible to separate the various organomercury constituents of a sample by gas chromatography (GC)[110, 115] or high performance liquid chromatography (HPLC)[116-118] prior to CVAFS. It is also possible to use the differing vaporization temperatures of the mercury species to separate them, then identify the various components as they boil off by inductively coupled plasma mass spectrometry, with the mercury vapor being trapped by a gold covered silica mesh post mass spectral analysis and later analyzed for concentration by standard CVAAS and CVAFS.[119] In all of these cases, the conversion of inorganic mercury to methylmercury during analysis can occur, potentially presenting a major problem. This can be corrected for by spiking the sample with isotopically labeled mercury at various stages in the preparation and analysis, then using the transformation that occurred to the spike as a guide to what has occurred to the actual sample.[111]

1.7 Mercury Remediation

Due to the significant threat of mercury pollution, the development of new remediation technologies is an active field. The majority of these efforts aim to remove mercury from wastewater, although some have also been targeted towards removal from the gas phase. These processes run the gamut from bioengineered plants to new chelation agents. Since the remediation of mercury is an ultimate goal of this thesis research, these technologies will be discussed in some detail.

1.7.1 Remediation of Mercury from the Gas Phase

The removal of mercury from the gas phase is a significant area of research. A major reason for this is the US EPA's decision to regulate mercury emissions from coal-fired power plants. There is a clear need to develop better technologies for trapping mercury from flue gas.[76]

One area of interest has been the removal of mercury from coal prior to its combustion. In fact, simply cleaning (by conventional, physical means) the coal prior to combustion can reduce its mercury content by an average of 37%.[77] This, however, is not good enough to satisfy the expected regulations. Furthermore, efforts in this area are greatly complicated by the fact that coals from different sites are contaminated by different mercury compounds, or at least by similar compounds in significantly different ratios. However, some general techniques have been developed.

For example, heating samples of Powder River Basin coal to around 290 °C prior to combustion will volatilize 70-80% of the coal's mercury.[120] This heating occurs in a specially designed reactor, where the volatile mercury could be recovered for disposal. However, higher temperatures were required to get comparable results for some other lignites and the process was not very effective for bitumous coal, suggesting that the coal's mercury was in a less volatile form. Another study also found that the percent mercury removed under pyrolysis conditions (up to 600 °C) varied dramatically with the coal sample studied.[121] Furthermore, it should be noted that around 400 °C, most coals undergo pyrolysis and their heating value consequently decreases,[120] suggesting that this method may not be very promising for most coals.

Another method of coal pretreatment is leaching. A recent study has found that a two-step procedure, in which the coal is initially soaked in a mildly acidic solution, then subsequently washed with hot (80 °C) concentrated HCl, resulted in the removal of 57-77% of the mercury from North Dakota lignite and 60% for Blacksville bituminous.[122] In another study, leaching by basic ligand solutions (including *meso*-2,3-dimercaptosuccinic acid (DMSA), 3-mercaptopropionic acid, and 2-mercaptoethanol) was found to have limited effectiveness, with the best results (57% Hg removal) being reported for DMSA.[121] Leaching with solutions enriched in sulfate-reducing bacteria have proven ineffective for mercury removal.[122]

Since none of the methods reported above were effective in removing sufficient mercury from the coal pre-incineration, it is clear that the remaining mercury will have to be trapped out of flue gas. This is a significant area of current research. One simple way of tackling the problem is to ensure that any mercury is in the less volatile Hg^{II} state and kept in the fly ash. This is often achieved by having low temperature burners and selective catalytic reduction units installed to lower the emission of NO_x and achieve flue gas desulfurization.[76, 123] However, while very helpful, this alone will not prevent the emission of impermissibly high amounts of mercury because it is very dependent on the mercury and carbon content of the coal (high carbon coals will trap more mercury in their fly ash).

The next step, therefore, is to find some adsorbent material through which the flue gas may be passed, removing its mercury.[76] Several adsorbent materials have been tried. In general, little success has been achieved with inorganic materials such as alumina[124] (although a recent study has shown great promise for thiol-derivatized alumina and silica sorbents[125]), molecular sieves[126], zeolite[127] (although there is a literature report of 63% mercury removal using what was described as a "treated zeolite", the treatment presumably being sulfur impregnation[124]), and bentonite.[127] Even after impregnation with sulfur (although it should be noted that sulfur impregnation was apparently effected by treatment with sulfuric acid or S_8, rather than by the addition of thiol groups), these compounds were ineffective. Good removal could be achieved, however, from the use of activated carbon, and removal became near quantitative for an extended period when the activated carbon was impregnated with sulfur, especially if the carbon was also treated with a small amount of potassium iodide.[128] Similar results have been reported when activated carbon is used to cleanse geothermal exhaust gas, with the added benefit that H_2S in the gas will sulfur-impregnate the carbon, permitting the pre-impregnation step to be skipped.[129] If an even lower cost sorbent is required, recent studies have shown that wood char is nearly as effective as activated carbon and sulfur-impregnated wood char has a usage lifetime nearly as great as sulfur-impregnated activated carbon.[127]

Since all of these processes involve the adsorption of mercury onto the adsorbent, they will eventually become saturated, and the adsorbent must be periodically replaced. Also, it is not surprising that long-term stability as well as removal efficiency increase upon the addition of sulfur; the process is transformed from physical adsorption to chemical adsorption. Mercury simply physisorbed to activated carbon may eventually escape, resulting in an equilibrium being reached between new mercury-containing molecules being adsorbed and old mercury-containing molecules escaping. Sulfur-bound mercury is unlikely to escape under these conditions, so the sorbent continues to function smoothly until it is saturated.

Flue gas from coal-fired power plants is not the only system where airborne mercury must be remediated. For example, crematoria exhaust can contain significant amounts of mercury due to the incineration of dental amalgams. One novel solution for this problem was studied in Sweden.[81] Ten grams of selenium in an aluminum ampoule contained in a wooden box was placed near the head of the coffin before it entered the furnace. If the system worked properly, the selenium would be released just as the mercury volatized, combining with the mercury to form mercury selenide. Although it proved difficult to conduct a good field test (it was deemed unacceptable to test the corpses for total mercury content prior to cremation), statistical analysis showed that significantly less mercury was emitted from the coffins treated with selenium, and controlled simulations (with selenium and mercury amalgam but no cadaver) suggest that as much as 85% of the mercury was bound by the process. However, there is some doubt as to whether the US EPA would permit a process that volatilizes selenium, which has its own toxicological problems, to be used in this country.

The trapping of airborne mercury is likely to remain a topic of significant research. Currently activated carbon appears to be the best technology available, especially if that carbon undergoes sulfur impregnation prior to use. However, there is room for further work in this field.

1.7.2 Remediation of Mercury from Water and Soil

At this point, before beginning a discussion of the most common remediation methods for soil and water, a few general points should be discussed. Many of the techniques that will be covered require significant infrastructure. The waste stream to be remediated must be made to flow through a certain filter or reactor so that the mercury can be removed. That is fine if the contaminated area is fairly localized, such as waste emanating directly from an industrial site or water entering a wastewater treatment facility. However, these technologies will be of little use for dealing with mercury that is already in the environment. For example, one cannot feasibly divert all the water of the Everglades through a processing site. This is an important fact to keep in mind when evaluating potential remediation technologies.

1.7.2.1 Excavation and Capping

Traditionally, the most common method of remediation for mercury-contaminated soils is excavation and disposal. The contaminated soil is manually removed and deposited in a hazardous waste landfill, roasted[130], or washed to recover the mercury.[131,132] Although this process has been widely used to deal with mercury contamination near broken gas pipe manometers, it is a fairly labor intensive and crude method. Furthermore, it is only useful if the mercury is tightly localized. If the contaminated soil is in a streambed or watershed, the analogue of excavation is dredging.[84] This contains all the problems of excavation, plus the stirring of the sediments inherent in this process can actually lead to a spike in the aqueous mercury concentration.

An alternative to dredging is capping. In this process, the contaminated stream or lake bed is simply covered by some blocking substance, such as sand, to prevent mercury in the soil from leaching into the water. Some studies have suggested that in the short term this may be a good way to contain mercury contamination before it can spread.[84] However, this is not a long-term treatment, since the original mercury is still in the system and will eventually leach out through the capping layer. Therefore, recent efforts have focused on developing more sophisticated long-terms technologies for water and soil contaminated with mercury.

1.7.2.2 Soil Heating

One of the interesting properties of mercury and its compounds is their volatility. Often this poses a problem, as it permits mercury to more easily escape and contaminate the environment. A recent paper, however, has suggested that this property can be used for the remediation of contaminated soil.[133] Simulated pollution sites were created in the lab and heated up to ~500K *via* UV lamps for ten days. Analysis showed that this procedure resulted in the removal of 67% of the soil's total mercury by evaporation. The authors of the paper hoped this procedure could be scaled up for *in situ* remediation of topsoil. Unfortunately, there are some apparent problems with this approach. The energy requirements to heat soil to these temperatures *in situ* could prove prohibitive; the authors propose to get around this problem by using solar or steam heat but neither approach has yet been found feasible. Furthermore, the mercury is not being collected by this method. The now volatile mercury will therefore enter the atmosphere and precipitate somewhere else, meaning that this approach comes closer to moving the problem around than actually solving it. This is a problem with several other mercury remediation schemes as well.

1.7.2.3 Phytoremediation and Bioremediation

One of the most elegant remediation ideas currently in the literature is phytoremediation, the use of plants to clean up pollution. In this process, a species of plant life is introduced to a contaminated area and cultivated there. The plants, in turn, absorb environmental contaminants and either detoxify or sequester them. Phytoremediation has already been exploited to clean up sites contaminated by a number of organic contaminants (including TNT, PCP, and trichloroethylene) and metals such as cadmium, nickel, and lead.[134, 135] There are species that can also safely hyperaccumulate mercury. One example is the water hyacinth, a species native to South America that has been introduced to the California coast.[136] Studies have shown that these plants can accumulate concentrations of up to 4435 ppb mercury in their roots and 852 ppb mercury in their shoots. It is believed that the mercury initially accumulates in the roots, where it is bound to carboxylate groups, then partially migrates to the shoots, where it is more tightly bound by sulfur biochelates. Further studies could presumably determine the time period required for the plants to become saturated with mercury, at which point they could be harvested and replaced by fresh hyacinths. However, this would still leave the problem of what to do with the mercury-saturated plants, which now constitute toxic waste. Also, if the plants are eaten before harvesting, they become a route for the mercury to enter the foodchain.[137]

The literature does contain reports of a solution to that problem. It was discussed earlier how some bacteria defend themselves against mercury by utilizing a collection of genes known as the *mer* operon. These genes code for a series of enzymes that can demethylate organic mercury to form inorganic mercury, then reduce the inorganic mercury to elemental mercury, which is then released. Through genetic engineering, biologists have now succeeded in transferring the operon to some species of plants, including tobacco, yellow poplar, and Indian mustard.[137-140] These species were shown to survive in mercury-spiked solutions and to eventually remove significant amounts of mercury from those solutions. The mercury absorbed by the plants was converted to Hg^0 and released, meaning that the plants did not become saturated and did not therefore need to be harvested. Although it was possible, in the case of the Indian Mustard, to force the plants to accumulate rather than release the mercury by treating them with ammonium thiosulfate, the authors felt that volatilization was more cost effective and did favor this as a remediation method.[137] However, there is a major problem with this approach. If the plants do not accumulate the mercury, it will be released into the atmosphere. The authors of the studies felt this was acceptable, even though the mercury will eventually precipitate somewhere else. A certain percentage of that mercury will presumably be methylated and find its way into the food chain, where it will be concentrated into higher predators and potentially threaten human life. For this reason, the current author humbly disagrees with the contention that volatilization is a good long-term remediation plan. In the case of mercury, dilution is not a solution.

Another technology similar to phytoremediation is bioremediation, the use of microscopic organisms to clean up pollution. In theory, this appears to be a very promising route. After all, in nature, some bacteria can convert inorganic and methylmercury to elemental mercury via the *mer* operon. It seems likely that these same bacteria could be used to remediate polluted sites. In particular, a system has been developed for the bioremediation of waste water streams emanating from chlor-alkali plants.[93, 141] The waste stream is enriched with a nutrient solution for the bacteria and diverted through a bioreactor, containing a large colony of the organisms. The flow is regulated such that the water will remain approximately three hours in the reactor, which is also designed to retain the reduced mercury. The treated water then passes through an activated carbon filter to remove any mercury not captured by the bacteria. The elemental mercury can be recovered from the reactor and reused. This process is relatively cheap and has been shown to effectively remove mercury from the water streams. A somewhat similar process has been used to convert HgS deposits on the bottom of Minamata bay to Hg^0.[142] The HgS was dredged from the bay floor, solubilized by a combination of 3M HCl and $FeCl_3$, and then the Hg^{II} was converted to Hg^0 by added bacteria, with the now volatile mercury being trapped as it evaporated. However, the process does have some drawbacks. The mercury concentration in the incoming wastewater must be regulated, for if it grows too high, the mercury will overwhelm the bacteria's defenses and kill them. Also, this technique requires an extensive reactor setup and is therefore not suitable for *in situ* remediation.

Another option is to modify bacteria so that they rely on some route other than the *mer* operon to detoxify mercury. This way, the bacteria would not necessarily volatilize the pollutant and no reactor would be required to capture the elemental mercury released. This has also been attempted by genetic engineering of the polyphosphate kinase (ppk) gene into some bacteria that already contained the mercury transport *mer* genes but not the reduction enzyme.[143] The ppk gene codes for the organism to create large amounts of linear orthophosphate polymers. Basically, this was engineered to replace the merA enzyme, so that when mercury levels grew dangerous within the bacteria, polyphosphate was synthesized. Apparently the phosphate chelated the mercury and prevented it from interfering with processes within the cell, granting the treated bacteria the ability to hyperaccumulate the metal. Further work led to the addition of more *mer* genes to the bacteria, giving them the ability to convert phenylmercury to Hg^{II}, followed once again by chelation by ppk-produced polyphosphate.[92] This is interesting, because a phosphate is not as good a ligand for mercury as a thiol, so it stands to reason that bacteria that produced thiol compounds instead of polyphosphate might be even more effective. This also has been tried, by engineering into *E.Coli* the *mer* mercury transport genes and genes to express metallothionein, a cysteine-rich, low molecular weight protein which is known to chelate heavy metals through its cysteine thiol groups.[144] The *E. Coli.* was placed in a reactor, and mercury-contaminated water was permitted to flow through. The bacteria removed mercury nearly quantitatively until saturation was reached. Although this was an excellent filter system, it did face problems similar to other filters, namely that it could be saturated and then would have to be replaced. However, it has recently been shown that a propagating colony of such transgenic *E.Coli* will thrive even in such mercury-contaminated conditions, suggesting that it might not be necessary to replace the bacteria in the filter.[145] However, bioaccumulating bacteria are probably not a good choice for *in situ* remediation because they will become part of the local food chain and could actually increase the bioavailability of the mercury.

1.7.2.4 Filtration

The idea of using what amounts to mercury filters to purify a waste stream is not limited to the area of bioremediation. To the contrary, this is one of the hottest areas of research in remediation technology, as judged by the many papers published on the subject. Before a detailed study of this area begins, several general factors concerning these filtration methods should be noted. They all involve either physically or chemically absorbing mercury to the filters. Therefore, the filters will eventually become saturated, with the result that they will have to be either replaced or regenerated. Either way, secondary mercury waste is created, although to a certain extent that is true of all remediation technology. Also, for a filter to be effective, the contaminated water must be made to flow through the filter, preferably at a controlled rate. This means filters are of very limited use outside of controlled environments such as wastewater disposal areas. Although some discussion has been made of their use for *in situ* remediation,[146, 147] except in areas where the pollution is extremely localized, this is not a practical solution.

After all, one can hardly filter the Amazon (although the sheer size and contamination level of areas like the Amazon or Everglades make any remediation a daunting task).

The standard mercury sorbent is activated carbon. This is somewhat surprising, as several tests show that, although activated carbons are reasonably effective at purifying vapor streams (see above), many are quite poor for aqueous mercury waste.[148,149] However, recent studies have demonstrated that some activated carbons with significant amounts of surface oxygen (such as those made from furans[150] or some plant waste[151]) are effective as mercury filters, as are sulfur-derivatized activated carbons.[152] Another low-cost filter material is fly ash from power plants. A recent study suggests that fly ash high in sulfur trioxide can be used to remove up to 81% of the mercury from a 602 ppm solution[153] (of course, that concentrated a mercury solution would still be very contaminated after removal of 81% of its mercury). Due to the wide availability of fly ash, this is a method worth pursuing and should be the subject of future studies.

Also popular as filters are artificial ion exchange resins,[149, 154, 155] usually utilizing sulfur-based groups to bind the mercury. A test of several of these resins against a standard activated carbon sorbent found that most resins tested were superior to the carbon, although under the conditions tested, none succeeded in lowering the mercury levels to legal limits.[149] More recently, a glass fiber coated with a thiol pendant polymer proved to be an extremely effective filter, reducing a 3-6 ppm mercury solution to below the permissible mercury concentration for drinking water.[156] Similarly good results, with near quantitative removal of mercury from 100 ppb solutions, has been achieved by using dithiocarbamate-derivatized silica-gel columns.[157]

Another type of mercury filter is polymer-supported crown thioethers. These are a very active area of research, even though there is literature evidence that macrocycles are not as effective for binding mercury as open chain compounds,[11] probably because it is easier to remove the mercury from a crown thioether and regenerate the filter. One excellent example is $[17]aneS_5$ attached to polystyrene-divinylbenzene through an amine linkage.[158] This polymer showed excellent extraction properties, with mercury removal rates of 99-97% after thirty minutes exposed to solutions of as high as 34 ppm mercury. An impressive 91% mercury removal rate was achieved in an extremely concentrated solution of 170 ppm mercury. The authors attributed the success of their compound to its increased hydrophilicity in acidic water stemming from the amine linker. The polymer could be regenerated expensively by treatment with diphenylthiocarbazone and reused.

Most of the polymers just mentioned could be regenerated by washing with acid. This presents a slight problem. If one treats the resin with HCl to remove the mercury, a new batch of mercury contaminated water has just been created. Disposal of this secondary waste could prove costly. In an attempt to get around this problem, filters have been developed that are regenerated by a thermally activated redox reaction.[148] These take the form of ion exchange compounds of the formula Li_xMS_2, the most promising being Li_xMoS_2. When a solution containing Hg^{II} passed through this material, it formed a black compound of the formula Hg_yMoS_2. If a 5-fold excess of the molybdenum sulfide salt was used, mecury removal was quantitative. This value could be used to calculate total possible mercury load, data that will have to be known if this is to be used as a practical mercury filter. Upon heating to 425°C, the mercury was released as mercury vapor (and trapped for reuse or disposal) and the MoS_2 was left behind. This could be reactivated with *n*-butyllithium and reused, although the moisture sensitivity of the *n*-butyllithium demands that some care be taken in this process.

Another approach to mercury filter design is to use mineral or mineral-like matrices as the filters. For example, a synthetic variant of the clay crandallite has been used as a mercury filter and found to lower the Hg concentration of a simulated waste stream from 70-90 ppm to

0.1 ppm,[159] although 0.1 ppm mercury is still a higher concentration than desirable. Perhaps a more obvious natural filter would be zeolites, which are already well known for their ion-exchange capabilities. Recent work has demonstrated that Sokornit zeolite filters can be used to lower the mercury concentration of a waste stream from approximately 0.15 ppm to 0.02 ppm,[160] although continuous addition of zeolite was necessary to maintain this concentration, casting some doubt on the practicality of this method. Other studies have suggested that mercury removal by zeolites can be dramatically improved by refluxing them for 36 hours with cysteamine hydrochloride or cystamine dihydrochloride, thereby adding thiol and disulfide groups to the zeolite, prior to use.[161]

This idea of functionalizing a mineral matrix to create a better mercury filter is a popular one, with mesoporous silica being a common reagent for these studies.[162, 163] The silica is functionalized with mercapto or chloroalkyltrimethylsilanes. In the case of the chloroalkylsilane, subsequent treatment with NaSH yielded the thiol derivative. A layer of thiol groups formed on the silica surface, converting the silica into a natural mercury filter. This compound proved very good at purifying simulated waste streams. At neutral or high pH, the silica filter could lower mercury concentrations (in ppm) by as much as four orders of magnitude. There was a slight decrease in efficiency at lower pH, due to protonation of the thiol, but this was not large enough to represent a serious concern. However, the silica was produced as micron-sized particles, which had to be immobilized by a second substance such as clay before use. A later synthesis succeeded in creating similar silica particles of macroscopic size, which performed as well as their micron-sized counterparts.[163] The functionalized silica could be regenerated with hydrochloric acid. Good results have also been gained using propylthiol functionalized mesoporous silica created by cocondensation.[164] Recent studies suggest that commercially available alumina, after functionalization with thiol groups, holds promise as a mercury sorbent.[165]

A silane condensation has also been used to attach thiol groups to montmorillonite, a smectite clay.[166] The resulting clay, called thiomont, was not as effective a mercury filter as the silica derivative, but still far superior to many activated carbons. Another clay, impregnated with 2-mercaptobenzimidazole, was later found to be capable of near-quantitative removal of mercury from waste streams under laboratory conditions, strongly suggesting that this could be a very cost-effective way of developing mercury filters.[167]

While not exactly mineral based, a somewhat related idea involves using mossy tin as a mercury filter.[168] The tin reduces Hg^{II} to Hg^0 and then forms an amalgam with the elemental mercury. This system was intended for *in situ* use in mercury contaminated groundwater. However, although it was quite effective at reducing the mercury, it was much less effective at trapping the elemental metal. It also leached tin into the environment. Therefore, this idea appears distinctly unpromising.

Another potential matrix for mercury filters is biopolymers. These are very attractive because they are potentially quite cheap. For example, cellulose can be brominated, then thiolated with NaSH and used as a mercury filter.[169] It proved effective, especially at slightly elevated pH. However, the cellulose could not be regenerated, even with hydrochloric acid. Corn stick powder and cellulose were both thiolated and used as a filter in a later study.[170] Both were also reasonably effective, always giving greater than 97% mercury removal. Another effective biopolymer is cross-linked carboxymethyl cornstarch.[171] This was prepared by the successive reaction of cornstarch with $POCl_3$, followed by sodium chloroacetate. It was capable of reducing a mercury solution from 208 ppm to 0.2 ppm. Yet another sorbent was prepared by the graft polymerization of acrylamide onto coconut husks; the addition of 2 g/L of the resulting biopolymer removed 99.4% of the mercury from a 25 ppm solution.[172] An even simpler biosorbent can be made by boiling the fungi *Aspergillus niger* in a solution of potassium hydroxide.[173] The resulting sorbent removed 90% of the mercury from a 20 ppm Hg^{II} solution and 60 % of the mercury from a 20 ppm $MeHg^+$ solution. More recently, the same group saw even better results with a filter made of ground coriander.[174] Due to their low cost and effectiveness, biopolymers are a potentially excellent source of mercury filters.

1.7.2.5 Complexation and Ultrafiltration

A method that has received recent attention in the literature and is somewhat intermediate between the filtration just discussed and the precipitation to be covered in the next section is the method of complexation and ultrafiltration. This method involves the addition of a water-soluble polymer (polyethylenimine in the studies cited) to complex the mercury, followed by filtration through a 15 kDa membrane.[60] The mercury-polymer complexes were too large to pass through the membrane and were therefore retained. Greater than 99% removal of mercury from 5-10 ppm solutions was reported. Furthermore, it is possible to recycle the polymer through electrolytic removal of the mercury, making this process potentially cost-effective.[175] However, due to the need to pass the mercury-polymer complex through a membrane filter, this process suffers from the infrastructure requirements inherent in a filtration method and therefore is not suitable for *in situ* remediation.

1.7.2.6 Precipitation and Extraction

Another method of removing mercury from water is to alter the solubility of the mercury components so that they will either precipitate or can be extracted from the waste stream. At its simplest, this just means reducing the Hg^{II} to the far less soluble Hg^0. Several ideas exist in the literature for doing this. One is to simply treat the mercury solution with powdered zinc metal.[176] The resulting spontaneous redox reaction will reduce all the divalent mercury in solution (equation 1).

$$Hg^{II} + Zn^{0} \text{ --> } Hg^{0} + Zn^{II} \quad (1)$$

This has been shown to effectively remove mercury from water. However, it is still necessary to recover the now metallic mercury, and to further treat the waste stream, which will now contain extremely high zinc levels. A similar idea is the photoreduction of mercury with a titanium oxide catalyst.[177] The catalyst works in the presence of sunlight, resulting in metallic mercury and Hg_2Cl_2 plating onto the TiO_2 particles. The metal contaminated catalyst can eventually be removed and treated with acid to regenerate useable TiO_2. This process will remove significant amounts of mercury, but it can be inhibited by the presence of Ca^{II} or Mg^{II} ions. Also, the elemental mercury generated on the catalyst must still be dealt with. Therefore, both these processes, while perhaps being useful for a waste-water treatment center, are not at all useful for *in situ* remediation.

Another idea is to add complexing surfactants, which will combine with mercury and other toxic metals and change their solubility so that they can be extracted into an organic solvent. In a recent study,[178] the surfactants used were commercially available compounds. Nitrogen- and oxygen-based ligands and organic solvents such as kerosene, decane, and 1-decanol were used for the extraction. This method proved to be quite effective and even successfully remediated samples of polluted wastewater from several sites. A similar method, utilizing the commercial reagent LIX 34 (4-dodecyl-N-8-quinolinylbenzenesulphonamide) in toluene, has successfully remediated mercury-contaminated sludge.[179] These techniques, however, do require some significant infrastructure, so they could only realistically be performed at a wastewater treatment site. They also generate new metal contaminated organic layers that must be dealt with. Therefore this author fails to see the advantage of the process over more simple precipitation methods, unless recovery of the metals is the objective.

That leads to one of the most popular methods of mercury extraction, the addition of a ligand to precipitate the mercury compounds. The structures of several metal precipitating ligands are shown in figure 1.6. One very popular ligand for these applications is sodium N,N-dimethyldithiocarbamate (DMDTC) (Figure 1.6a).[180] This compound forms insoluble complexes with mercury, which precipitate and can be removed from water. It has been shown to be effective at removing mercury from mixed gold/mercuric cyanide waste streams, among other applications. However, the long-term stability of these precipitates is very questionable. Studies have shown that the addition of DMDTC to mercury contaminated water will result in an immediate drop in the mercury level. However, within hours the mercury level will begin to rise again if the precipitates are not removed from the water, suggesting that the mercury is leaching back out.[181] Also, DMDTC is known to decompose into byproducts, such as thiram, which are toxic to fish.[181] Therefore, while useful for wastewater treatment sites, this compound is clearly a very poor choice for *in situ* remediation.

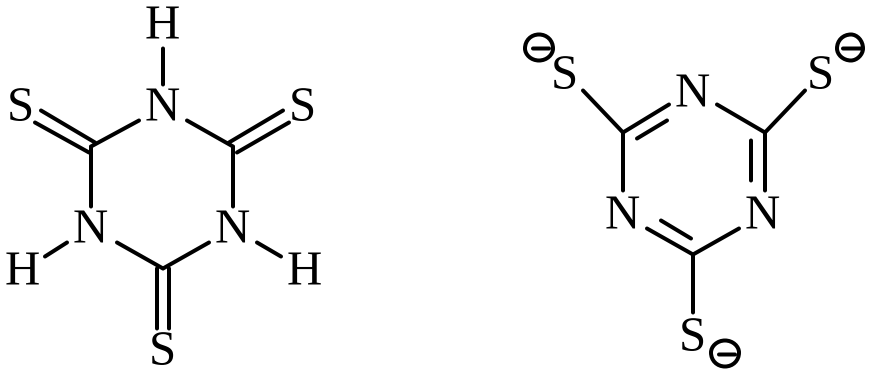
Another commercial precipitating agent is sodium trithiocarbonate (STC) (Figure 1.6b). This compound has also been shown to precipitate mercury, albeit not quite as effectively as DMDTC.[181] However, there is once again a serious problem with the long-term stability of the resulting complexes. Apparently STC does not bind mercury as the expected trithiocarbonate complex, but rather decomposes into cinnabar and carbon disulfide. As has been mentioned above, cinnabar is a potential source of mercury for methylation, so its precipitation into the environment is not a good solution to mercury contamination. Furthermore, carbon disulfide itself is a toxic compound, so in the attempt to remediate one pollutant, this compound creates another. Therefore, STC is completely inappropriate for *in situ* remediation of contaminated sites.

1.8 Mercury Precipitation Research in the Atwood Group

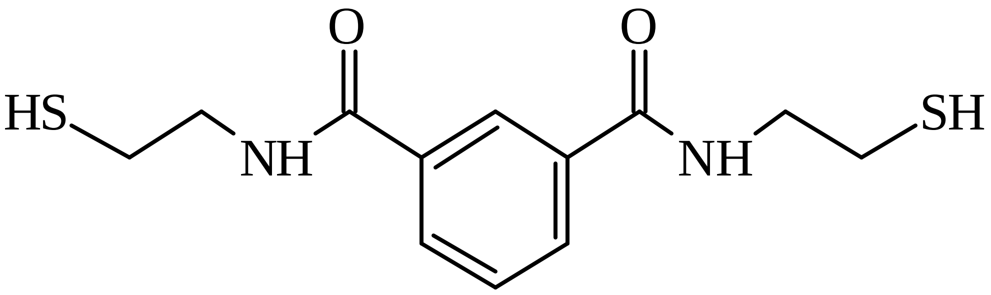
A third commercially available metal precipitator, which as been studied in some detail by the Atwood research group, is the sodium salt of 2,4,6-trimercaptotriazine (sodium 1,3,5-triazine-2,4,6-trithiolate, TMT). Although, it has been used to precipitate a number of metals from contaminated waters, the basic chemistry of TMT was not well understood until recently.[182] TMT is an easily tautomerized triprotic acid, with its fully protonated form actually being a thione with the hydrogens on the nitrogens and C=S double bonds (figure 1.6c), while the trisodium salt contains anionic sulfurs and C=N double bonds (figure 1.6d). Although the sodium salt is highly soluble in water, the fully protonated form is insoluble. Therefore, the compound's usefulness as a remediation agent is closely tied to its degree of deprotonation. However, only two of the three acid dissociation constants were previously reported in the literature.[183] These were slightly suspect because the protonated form's reaction with pyridine resulted in the formation of a mixture of monodeprotonated (H_2TMT^-) and fully protonated TMT (H_3TMT), when the reported pK_{a1} was sufficiently acidic that only the H_2TMT^- form should have been present.[184] Therefore, the author's first assignment upon joining the group was to accurately determine the disassociation constants for TMT.

It is a relatively simple procedure to determine the pK_a (the negative log of the acid dissociation constant) for an acid; it is the pH at the half-way point (by volume) between the start of the titration and the equivalence point (the point at which the basic titrant has completely neutralized the acidic analyte). This holds true for multiprotic acids as well.[185] In the titration of

a. DMDTC b. STC



c. TMT (thione) d. TMT (thiolate)



e. BDET

Figure 1.6: Commercial remediation agents

a triprotic acid with a base, the first pK_a will lie halfway between the start and the first equivalence point, the second pK_a will be halfway between the first equivalence point and the second equivalence point, and the third pK_a will be halfway between the second and third equivalence points. A complicating factor here is that the fully protonated form of TMT (H_3TMT) is highly insoluble in water; therefore, rather than use a base to titrate the weak acid, an acid was used to titrate the trisodium salt (used as a nonahydrate) of TMT. This is a perfectly legitimate method for calculating these pK_a values. The Henderson-Hasselbalch equation (equation 2) shows that the pH will be equal to the pK_a for any system containing equal concentrations of a weak acid and its conjugate base. It does not matter whether one achieves

$$pH = pK_a + \log ([\text{Base}]/[\text{Acid}]) \qquad (2)$$

that equal concentration by adding base to the acid or another acid to the conjugate base.

Ten titrations were performed, five using aproximately 50 mM K_2SO_4 to ensure a stable ionic strength and five with no background electrolyte. No significant difference was observed between the two sets of data, so they were combined to calculate average pK_a values. A representative titration curve is shown in figure 1.7. The result was an average value of 5.71 for pK_{a1} ($H_3TMT \rightleftharpoons H_2TMT^-$), 8.36 for pK_{a2} ($H_2TMT^- \rightleftharpoons HTMT^{-2}$), and 11.38 for pK_{a3} ($HTMT^{-2} \rightleftharpoons TMT^{-3}$). These new values were used to create a fractional composition chart, showing what fraction of the acid is in each form at a given pH (figure 1.8). This information could be then used to make TMT-metal complexes with vaying degrees of protonation.[182] The synthesis of these compounds confirmed the accuracy of the new pK_a values.

Unfortunately, TMT is less effective for mercury precipitation than many of the ligands discussed earlier.[181] Furthermore, the resulting precipitate is a white gel which upon drying will form either an amorphous green or yellow solid, a white crystalline solid, or a gray crystalline solid.[186] Over the course of a year, most of these solids ultimately convert to the gray crystalline form, releasing mercury during this transformation. The preliminary forms (white crystalline and amorphous yellow) also leach significant amounts of mercury.[186] Although the exact composition of these precipitates or the process by which they interconvert is not well understood, it is clear that the precipitates are not stable enough to be left in the environment, making this compound of little use for *in situ* remediation.

No discussion of mercury remediation technology would be complete without at least mentioning the BDET ligand (a benzene backbone with with two terminal thioalkyl amide arms, figure 1.6e) developed in the Atwood research group.[187, 188] This ligand has proven very effective at removing mercury from water and has been successful in remediating both lab and field samples. When a 10% excess of ligand was added to a 50 ppm mercury solution, it reduced the concentration to 0.02 ppm.[187] In a field test, the BDET ligand lowered the mercury concetration of a waste stream from an active gold mine in Peru from 34.5 ppm to 0.008 ppm.[189] The ligand was also used to treat some heavily contaminated soil samples provided by the Kentucky West Virginia Gas Company.[190] On average, these samples contained an immense concentration of 10300 ppm mercury, which was reduced to 40 ppm upon treatment with a peroxide solution (to oxidize the mercury to Hg^{2+}) followed by addition of a 55% excess of BDET solution.[190] The ligand-mercury precipitates have also proven stable to leaching.[190] To the best of this author’s knowledge, this is the most effective ligand for mercury removal currently reported. However, it should be noted that these are essentially bidentate ligands and would be expected to bind mercury in a linear geometry. The major hypothesis of this thesis is that flexible, tetradentate chelates will prove to be equally or even more effective ligands for mercury precipitation than BDET.

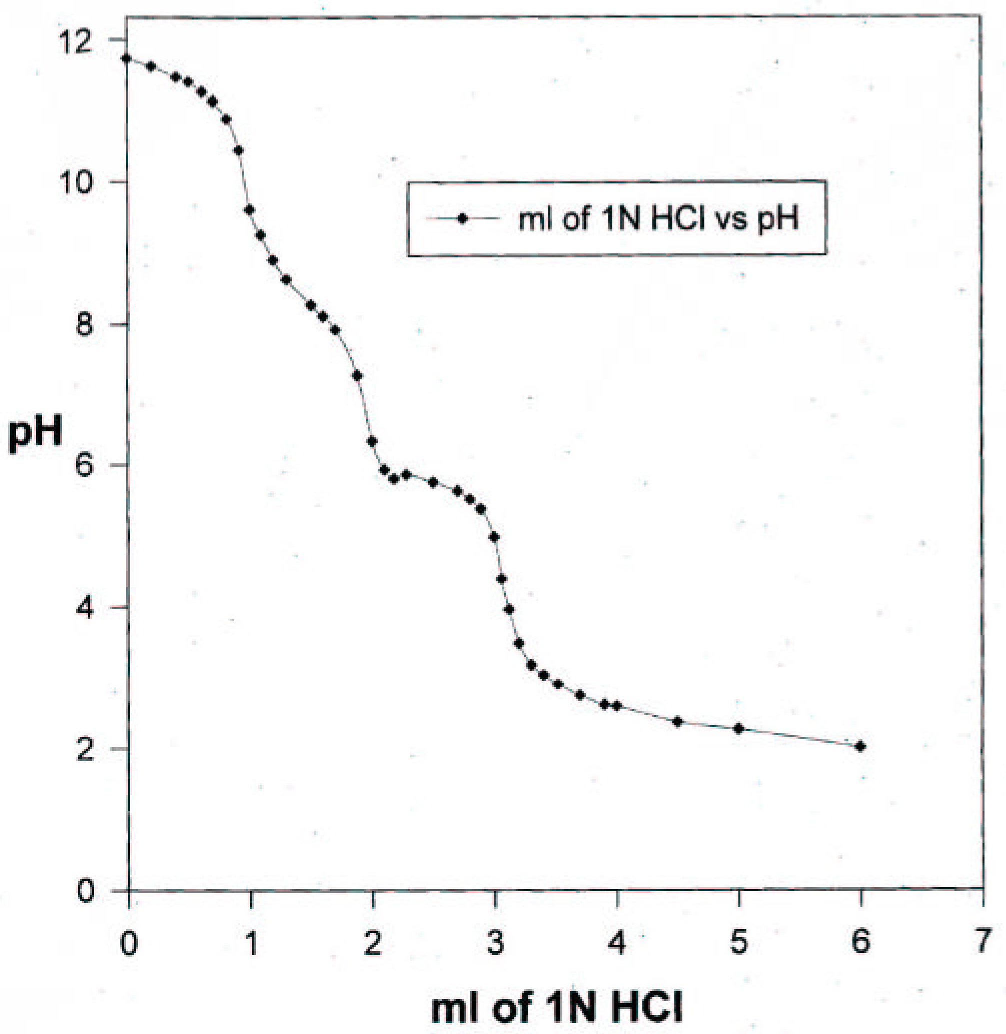


Figure 1.7: Representative TMT titration curve

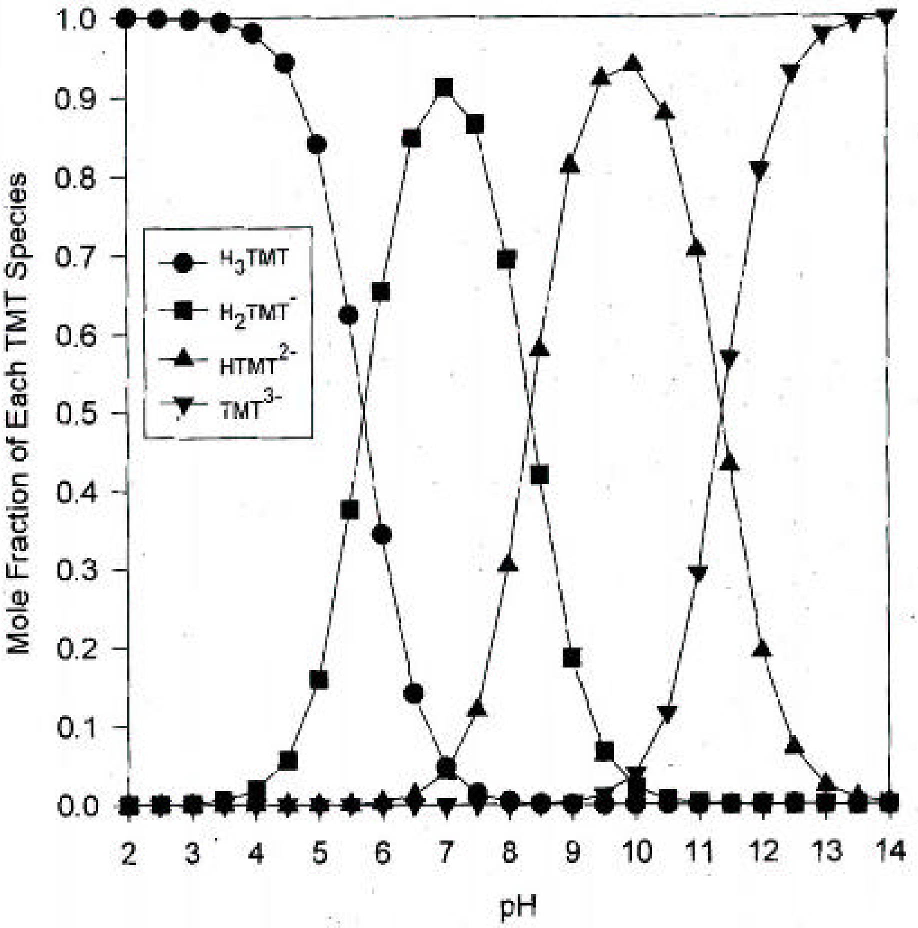
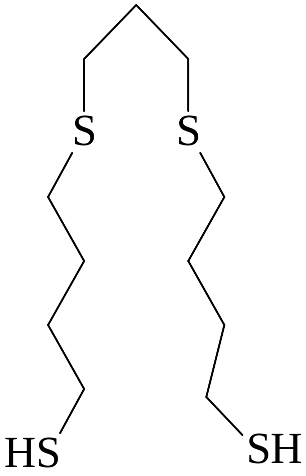


Figure 1.8: Fractional composition of TMT by pH

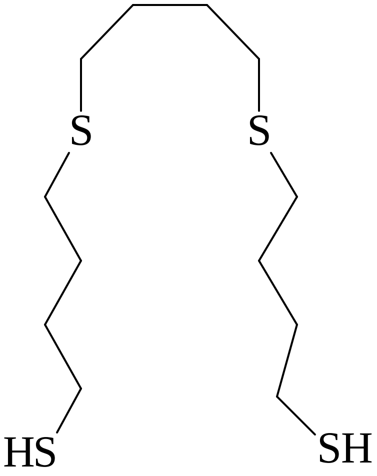
1.9 The Design of an Ideal Mercury Precipitation Agent.

It is the goal of this thesis research to design a series of new compounds for the precipitation of mercury from contaminated waters. The thesis is based on the hypothesis that a four-coordinate sulfur-containing ligand of sufficient size to form a tetrahedral coordination environment around mercury would successful remove mercury from water and yield stable precipitates. Due to the strong covalent bonds that mercury forms with sulfur, this ligand should sulfur-based. It should be an open-chain molecule, not a macrocycle, because it has already been established that open-chain ligands tend to form more stable mercury compounds than sulfur macrocyles.[11] Moreover, the ligand should form covalent bonds with mercury, a bonding situation that can not be achieved with a macrocycle. Furthermore, this compound should be large enough to assume a tetrahedral geometry around mercury.[14] As discussed above, a macrocycle must have at least 16 members before a mercuric ion can fit into its cavity.[15] This is the equivalent of saying that at least three carbons must separate each sulfur. Even though the ideal ligand is expected to achieve tetrahedral, rather than square planar, coordination to mercury, this spacing of the sulfurs seems reasonable, so a minimum of three carbons between sulfurs becomes a requirement. When all these factors were taken into account, the resulting hypothetical ligands, 5,9-dithio-1,13-tridecanedithiol (3S4SH) (Figure 1.9a) and 5,10-dithio-1,14-tetradecanedithiol (4S4SH) (Figure 1.9b**)** were deemed good first targets for an ideal mercury remediation chelate.

To save space, the author has developed a simplified and unofficial nomenclature for these compounds, all of which basically consist of an alkyl backbone with the same heteroatom at each end, with an alkyl chain arm extending from each heteroatom, ending in some functional group . These "nicknames" designate each compound with a short series of numbers and letters. The first number is the number of carbons in the backbone, which is followed by the element in



a. 3S4SH



b. 4S4SH

Figure 1.9: Target ligands for the ideal mercury precipitation chelate

the backbone, then the number of carbons in the arm, finally the terminal group of the arm. Hence 5,9-dithio-1,13-tridecanedithiol is designated 3S4SH. In this work, compounds will initially be identified by their IUPAC name and nickname, then the nickname alone will subsequently be used.

Experimental Section

Determination of the Acid Dissociation Constants of H_3TMT: All pH measurements were taken using an Orion model 710A pH/ISE meter with an Orion 8102BN Ross combination electrode. The meter was calibrated with pH 4.01, 7.00, and 10.01 Orion standards at 20-25 °C. The titrations were performed by measured addition of 1.0 N HCl to 6.38-9.79 mM aqueous solutions of purified $Na_3TMT \cdot 9H_2O$ (Degussa Corp., purified by recyrstalization from 1:2 water ethanol mixture), with concurrent monitoring of pH. The data was plotted and curve-fit using *SigmaPlot* (Jandel Scientific, San Rafael, CA) and the equivalence points determined by taking the second derivative of the curves.

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Chapter Two: Non-Thiol Ligand Byproducts of the Project

2.1 An Introduction to Sulfur

An ideal mercury chelation ligand should be sulfur-based, so a brief discussion of sulfur chemistry is appropriate at this point. Ground- state sulfur has the electron configuration [Ne]$3s^23p^4$ and a Pauling electronegativity of 2.5, the same as carbon and iodine. It also has possibly the most extensive allotropy chemistry of any element,[1] due to catenation through strong element-element covalent bonding.[1, 4] The most stable of these allotropes is orthorhombic S_8. Sulfur also is found in a wide variety of oxidation states, the most common being –2, -1, +4, and +6.

Sulfur is known for its distinct "rotten eggs" smell, and many organosulfur compounds also possess odors that are unpleasant, often extremely so. In fact, the "musk" secreted by skunks is a mixture of several organosulfur compounds, including 2-butene-1-thiol, 3-methylbutanethiol, 2-butenylthioacetate, 3-methyl butanylthioacetate, 2-phenylethanethiol, 2-quinolinemethanethiol, and 2-quinolinemethanethioacetate.[191] The skunk-like stench of organosulfur compounds, detectable even at very low concentrations, presents a special challenge to chemists working with them. The best way of dealing with this odor is to treat the contaminated item with bleach (sodium hypochlorite), which converts the thiols to less foul oxidized products. In practice, the stench associated with these compounds makes it nearly impossible to remove them, or anything that has been in contact with them, from the fume hood.

Sulfur is the sixteenth most abundant element and occurs in nature in a variety of forms. Historically, it has long been an important element. It is mentioned in the Bible, the writings of Homer, and the *Natural History* of Pliny the Elder. It was one of only two nonmetallic elements known to ancient man.[1] Along with mercury, sulfur was a key element for the alchemist. Sulfur, in combination with charcoal and potassium nitrate, formed gunpowder, obviously one of the more important chemical compounds in human history.[6]

Sulfur remains a key element for human industry. Approximately 90% of all sulfur used goes into the production of sulfuric acid,[4] which is manufactured in greater quantity than any other industrial chemical and has a variety of industrial uses in every field from fertilizer production to metallurgy.[1] Beyond the manufacture of sulfuric acid, sulfur compounds have several other major industrial uses. Sulfur dioxide is an excellent preservative and widely used for wine preservation. Elemental sulfur or dithiocarbamates are used for the vulcanization of rubber. Sulfonamides are a major class of antibacterial drugs, while penicillin, possibly the world's best known antibiotic, is also an organosulfur compound. Sulfonic acids are important as dyes and detergents.[4]

Sulfur is a key element in the human body. Several major biomolecules, including the amino acids methionine, cysteine, and its disulfide cystine, contain sulfur.[4] Cysteine is of particular interest because of its terminal thiol group. When proteins are formed from this amino acid, they often contain pendant thiols. One example of this is metallothionein, a sulfur-rich metal-binding protein.[144] Furthermore, if two cysteine thiols from different proteins (or the same protein twisted over on itself) are in close proximity to each other, they can be oxidized to form a disulfide bond. This is one of the major structure-determining interactions in proteins. A great many biological redox reactions are centered on iron-sulfur clusters, a fascinating subset of bioinorganic molecules that is a major area of current research.[192] Sulfur also forms interesting biological complexes with copper,[193] zinc,[194, 195] molybdenum,[196] nickel[197] and a variety of other metals. In fact, it is partially due to the biological importance of sulfur that mercury is so dangerous; mercury will bind biological sulfur molecules and prevent them from performing their main functions.[198, 199]

Sulfur is in some ways chemically comparable to oxygen, the element above it in the periodic chart. For most common organic oxygen molecules there is a sulfur analogue. However, there are several key differences between the elements and their compounds. Thiols tend to be more acidic (pK_a PhSH~7.5 vs PhOH~10)[200] and better nucleophiles than alcohols. Sulfur also has access to an empty 3d orbital, which has been credited with permitting it to expand its octet. However, MO calculations suggest that the 3d orbitals actually play little role and that three-center, four-electron bonds are involved instead.[201] On the other hand, a number of these hypervalent sulfur molecules show an unusual stability that suggests the d orbitals may be playing a part after all.[4]

The vacant d orbital is also credited with permitting sulfur to form what has been termed $p\pi$- or $d\pi$-$d\pi$ type π bonds. This sort of bonding may play a part in the unusual affinity of sulfur for mercury. Mercury possesses a filled d shell, meaning that it has electrons available to donate into sulfur's empty d orbitals. Therefore, mercury probably forms what could be viewed as almost a π bond with sulfur. This sort of interaction has been put forward as a theoretical basis for the hard-soft acid base effect.[3] This also could be viewed as a form of back-bonding, not unlike that found with carbon monoxide and some later transition metals.

Sulfur is nucleophilic in its thiol form, a property that will be widely used in the research described in this dissertation. However, when combined with more electronegative elements, it can also be electrophilic. In fact, it is possible to perform nucleophilic attacks on sulfenyl and sulfonyl halides.[4] With sulfoxides, it is preferable to draw a resonance structure with a monovalent, formally negative oxygen and a trivalent, formally positive sulfur. In fact, it is not particularly unusual to find trivalent, positive sulfonium salts, which are readily formed by the attack of the sulfur lone pair on an alkyl halide.[4] This fact led to some difficulties with the author's research, as will be described later. In summary, sulfur has a rich and unique chemistry, which makes it extremely versatile as a synthetic reagent and its ability to form strong bonds with mercury makes it an ideal element to incorporate into mercury-binding ligands.

2.2 Diol Ligands

One possible route to the 3S4SH or 4S4SH chelates would be to synthesize the corresponding diols, 5,9-dithia-1,13-tridecanediol (3S4OH) and 5,10-dithia-1,14-tetradecanediol (4S4OH) and attempt to convert those species to the dithiols. The major attraction of this route was the apparent ease of synthesis of the diols. These compounds appear to be readily accessible by the reaction of dithiols with ω-halogenated alcohols. Furthermore, the diols could be potential environmental remediation ligands in their own right, not for mercury, but for hard acid cations of concern such as chromium or copper.

The literature contains a clear, and initially promising, method for the synthesis and thiolation of such diols. Rosen and Busch had synthesized a 3S2OH compound, which they then converted to 3S2SH as a precursor to sulfur macrocycles (figure 2.1).[202] In fact, this work was the original inspiration for the thiol ligands in this thesis. The thiolation was achieved with a twelve-hour reflux with thiourea in concentrated HCl and basic workup. Although the exact mechanism for this reaction was not available in the literature, a Japanese paper reported a dehydration product as an intermediate.[203] The authors implied that the reaction involved essentially an S_N1 attack (although an S_N1 mechanism is highly unlikely on a primary alcohol, the claim was supported by the fact that tertiary, benzylic, and allylic alcohols gave far better yields) to generate a thiourea-pendant compound, which is then hydrolyzed to the desired thiol by basic aqueous solution. However, in the case of a 1° alcohol, it is far more likely that a cyclic sulfonium intermediate was formed, then underwent ring-opening and thiolation by the thiourea. As it seemed possible that this reaction would work for the 3S4OH ligand, the route was pursued.

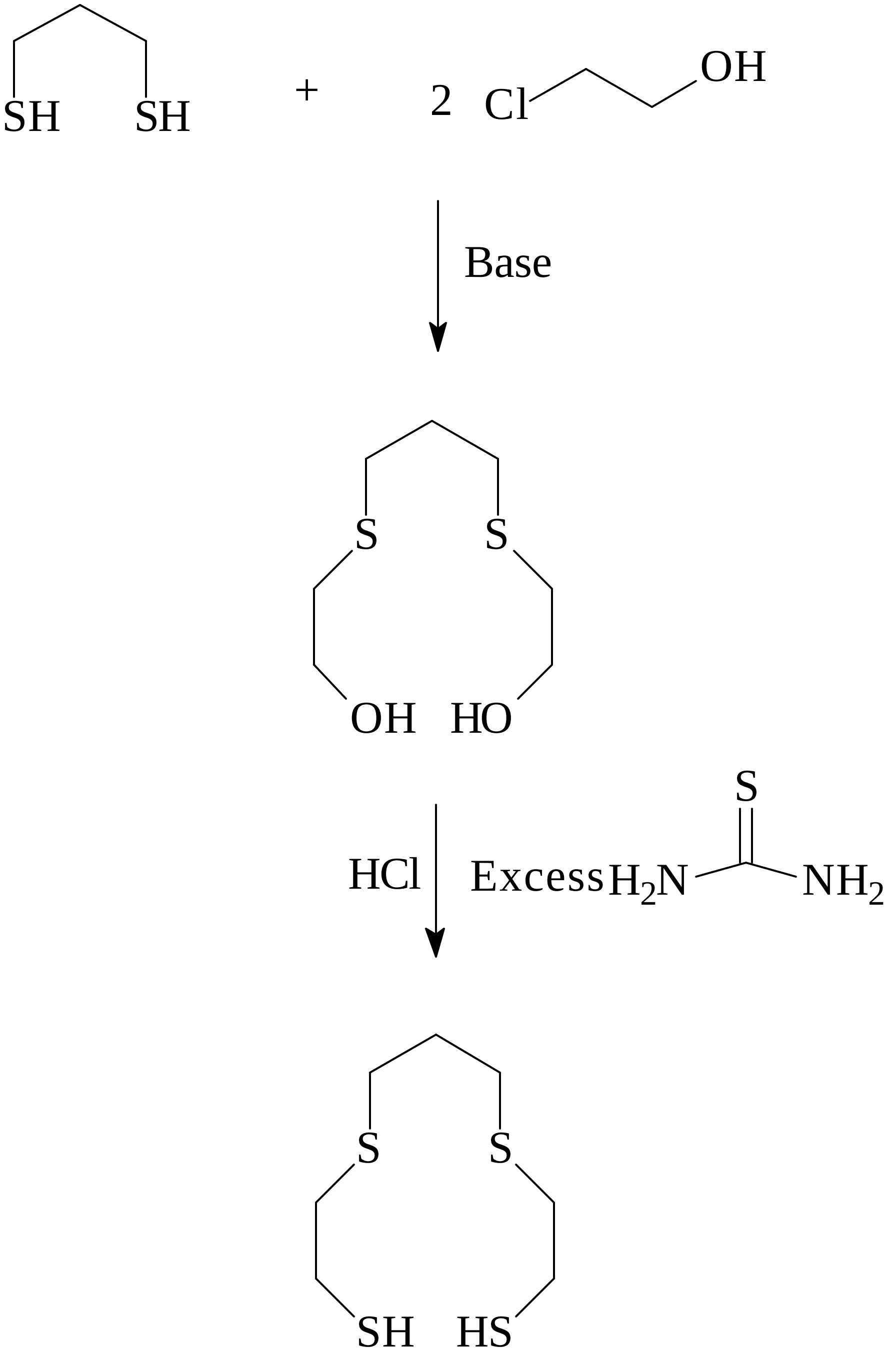


Figure 2.1: Rosen and Busch’s synthesis of 3S2SH

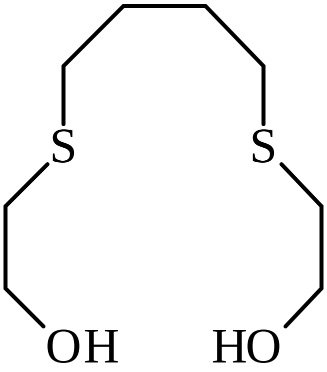
The starting point to making this a viable route to the 3S4SH class of ligands was to repeat Rosen and Busch's original work. The first step, therefore, was to synthesize their precursor 3S2OH. This was accomplished by combining propanedithiol and sodium ethoxide with two equivalents of 2-chloroethanol. The reaction went smoothly, with a 55% yield. The next step was to thiolate the diol with thiourea. This was accomplished by combining the thiourea and diol in concentrated hydrochloric acid under strongly forcing conditions (12-hour reflux). The acid solution was then neutralized with excess base, refluxed for three more hours, and worked up to yield the desired product, 3S2SH in 54% yield. The overall yield for the reaction, from start to finish, was 30%.

The next step was to adapt this synthesis to make the desired ligands. It appeared that this could be easily accomplished by simply substituting 4-chloro-1-butanol for 2-chloroethanol in the 3S2SH synthesis. However, there was one problem with this change; the 4-chloro-1-butanol could decompose into THF and HCl. Therefore, the starting material had significant decomposition problems and a limited shelf life after purchase. The reaction was still attempted, however, under the conditions described in the previous paragraph, and 3S4OH was produced. However, possibly as a result of the decomposition of the starting material, the best yield that could be obtained for this compound was approximately 40%.

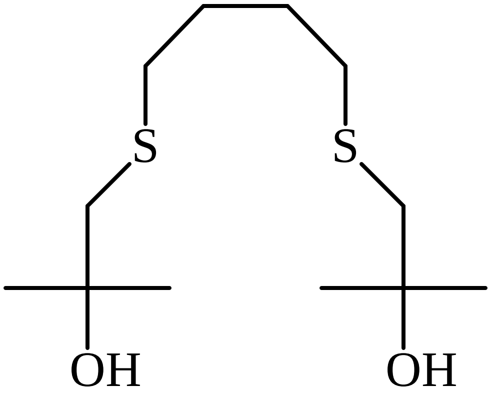
Conversion of the diol to the dithiol was attempted under the same conditions as for 3S2OH. However, although tried multiple times, this reaction never resulted in producing any appreciable amount of 3S4SH. Rather, a complex mixture of decomposition products usually resulted. Analysis by GC-MS showed that the major constituents of the mixture were propanedithiol and a form of 3S4SH missing one side-chain. This suggested that the diol had been successfully thiolated, but that the resulting compound was not stable under these conditions against decomposition to tetrahydrothiophene. Therefore, this route was not likely to prove an effective method for synthesizing 3S4SH or 4S4SH.

However, it had been demonstrated that diols could be synthesized with two sulfide linkages separated by three or four methylene groups in the backbone. These compounds had potential as metal chelates (albeit not well-suited for mercury) and were therefore pursued. To this end, the synthesis of a series of similar diols was attempted. The first of these to be created was 3,8-dithia-1,10-decanediol (4S2OH) (figure 2.2a). The synthesis of the ligand was achieved by the reaction of butanedithiol with two equivalents of chloroethanol and a three hour reflux. Standard workup gave the diol (a white, low melting solid) in good yield. Alternately, 4S2OH could be prepared by adding two equivalents of 2-mercaptoethanol to sodium hydroxide, followed after thirty minutes by the addition of one equivalent of dibromobutane. Once again a three hour reflux and the same workup yielded the product. Also a *gem*-dimethyl (tertiary) diol, 2,11-dimethyl-4,9-dithia-2,11-dodecanediol (4S2-*tert*-OH) (figure 2.2b) could be made from the reaction of two equivalents of chloro-*tert*-butanol with butanedithiol and excess base, while a variation of 4S2OH with three carbons in the arm rather than two, 4,9-dithia-1,12-dodecanediol (4S3OH) was made by substituting 3-chloropropanol for 2-chloroethanol in the 4S2OH synthesis.

Group thirteen chemistry has long been an area of interest in the author's research group. Although a number of applications, including the use of tetrazole ligands with aluminum alkyls as precursors to aluminum nitride,[204] the reactions of alkyl alcohols with aluminum and gallium alkys to form "Mitsubishi" molecules as precursors to solid-state materials,[205] and alumina-pepsin nanoparticles[206] have been explored, most of the work has focused on the salen family of ligands.[207-212] These are formed by the condensation of a diamine with two equivalents of a salicaldehyde-derivative and are diphenol, diimine ligands. They are tetradentate, bonding with



a. 4S2OH



b. 4S2-*tert*-OH

Figure 2.2: Some new dithioether diols

both the phenolic oxygens and the immine nitrogens. When combined with an alkyl allumnim or gallium species under air and moisture sensitive conditions, the hydroxyl groups will easily add to the metal, liberating alkane gas in the process. The resulting compounds have the metal in a five-coordinate environment, with either a square pyramidal or trigonal bipyramidal geometry. In light of the author's contention that flexible ligands will permit an ideal geometry around a metal (a central concern in the design of the mercury chelates), it should be noted that the trigonal bipyramidal geometry is favored, but can only be achieved by a ligand with at least three methylene groups separating the imine nitrogens.[212] This is comparable to the flexibility required for a thiol ligand to assume a tetrahedral geometry around a mercury ion. The five coordinate salen-aluminum compounds are useful as catalysts for the living polymerization of oxiranes. [212] Dialkyl aluminum chloride compounds will react similarly with salen ligands, eliminating the alkyl groups and generating a five coordinate species with chlorine still attached to the metal. This will undergo further reaction with Lewis basic solvents[208, 212] or gallium trichloride [210, 211] to yield cationic compounds which also act as catalysts for ring opening polymerizations.[208] One of the author's early projects in the group involved a related compound referred to as a "half-salen" ligand, which was synthesized by the reaction of one equivalent of 3,5-di-*tert*-butylsalicaldehyde with *tert*-butylamine. This ligand was bidentate and formed four coordinate compounds with a number of alkyl aluminum, gallium, and indium species.[213] Therefore, the author was well aware of the great reactivity between hydroxyl ligands and group thirteen alkyls.

To study the reactivity of one of the new diols with alkyl aluminum species, the 4S2-*tert*-OH ligand was combined in a 1:1 ratio with trimethylaluminum. Upon addition of the organometallic compound, gas evolution was visible, and a clear solid was produced. The compound was refluxed for 1 hour to ensure complete reaction, and then purified by cannula filtration under dry N_2 while still hot.

Although this compound proved too insoluble for NMR analysis, it was characterized by IR, mass spectroscopy, and elemental analysis. The IR spectrum resembled that of the original ligand, except for the absence of the strong O-H stretching band found in the protonated alcohol. This suggests that the hydroxyl groups have performed the expected methane elimination with the metal alkyl and the ligand is now bound to aluminum with its backbone intact. The mass spectrum, while not containing a molecular ion, showed a fragmentation pattern consistent with a structure containing one ligand bound to one AlMe. The elemental analysis confirmed this. The observed carbon content was less than 1% lower than the calculated value, while both the hydrogen and sulfur were within the instrumental uncertainty (0.5%) of the calculated values. Therefore it seems clear that this *tert*-butyl ligand formed a simple 1:1 compound with the aluminum (figure 2.3). Although the possibility of dimerization for this compound can not be fully discounted on the basis of the current data, there were no peaks in the mass spectrum of sufficient size to indicate dimerization. The formulation of one ligand, one aluminum, and one alkyl group is markedly different from the structures yielded by the reaction of ethylene glycol with alkyl aluminum (dimers with one of the four oxygens still protonated leaving one metal with two alkyl groups and the other with one or compounds of the formula $Al_3R_5(OCH_2CH_2O)_2$).[214] Similar monomeric compounds have been reported from the reaction of salen diols with alkyl aluminum[209] and dimethyl aluminum chloride,[211] however, so this is not an unexpected result for this reaction.

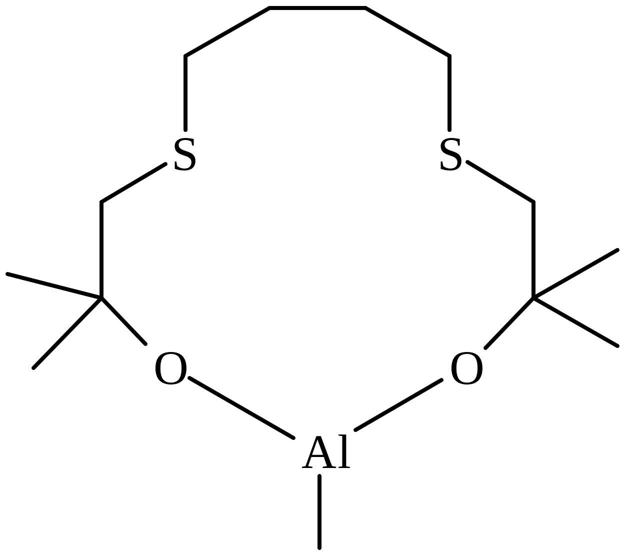


Figure 2.3 Proposed structure for 4S2-*tert*-OAlCH$_3$

2.3 Diene Ligands

Another possible route to the desired dithiol ligands, such as 3S4SH, was to start with the corresponding diene, convert this to a dithioacetate, which would then be transformed into a dithiol. The free radical addition of thiolacetic acid to alkenes was first reported in1939[215] and has been well studied since.[216-218] The reaction results in the anti- Markovnikov addition of an acetylthio group and in some cases occurs without the addition of any initiator beyond visible light.[215] More often, the free radical reaction is initiated by AIBN,[218] *tert*-butyl hydroperoxide,[217] or UV light.[219] Titanium tetrachloride has also been reported as a Lewis acid catalyst for thiolacetic acid addition to methacryloyloxazolidinones[220] (unlike the other reactions being discussed, this one does not proceed by a free-radical mechanism). These reactions have been conducted at elevated temperatures when ambient light[215] or AIBN[218] were used as the initiator, but with other initiators usually proceed at room temperature. Generally, the initiator used depends on the situation, although a UV lamp appears to be the most reliable system. In some, but not all, cases, the reaction is reported as being highly exothermic, usually after a brief induction period.[216, 217] A survey of the literature did not reveal any cases of the free radical coupling occurring in dienes. However, could this be achieved, then there are multiple literature methods reported for converting thioacetate groups to thiols,[216, 219, 221-225] holding out promise that the dithioacetate compounds targeted could be converted into the desired dithiol ligands.

The first step in this process would be the synthesis of the appropriate dienes. These should have three- or four-carbon backbones and four-carbon arms. Unfortunately, such compounds would presumably use as a precursor a 4-halo-1-butene, a commercially very expensive class of reagent. A version with three carbons in the arm, however, could presumably be made from the reaction of a dithiol with allyl bromide, which is cheap and easily obtained. If the reactions were successful utilizing ligands with three carbon arms, then efforts could be made to synthesize the halobutene precursors to a four-carbon-arm analog. The bis(thioacetate) ligands that would result from these reactions could then be converted to the desired dithiols (figure 2.4).

The dienes were readily synthesized. In the presence of two equivalents of base, excess allyl bromide readily reacted with 1,4-butanedithiol and mercaptoethyl ether to yield 4,9-dithia-1,11-dodecadiene (4S3diene) **(**figure 2.5a**)** and 7-oxo-4,10-dithia-1,12-tridecadiene (2O2S3diene) **(**figure2.5b**)**. The yields were 85% (for 4S3diene) and 87% (for 2O2S3diene). These compounds were clear oils at room temperature, with odors that, while not pleasant, were much less offensive than their thiol precursors.

Unfortunately, the efforts to convert these compounds to dithioacetates (using both AIBN and a UV light source) proved unsuccessful. In a typical reaction, the reagents were combined in hexane in a quartz test tube and were stirred under irradiation from a 15W UV light. Although a single addition product was often recovered, no appreciable amount of the desired double addition product was created. However, the work did result in the synthesis of a number of new dienes, the chemistry of which could be studied. Alkenes and dienes are very common ligands in organometallic chemistry, and the dithioether functionality of these compounds promised to make them even more interesting for reaction with metals. To explore the possibility of creating new metal complexes with these ligands, 2O2S3diene was combined with tin (II) chloride.

Organotin compounds are very important in modern organic synthesis. Tributyltin hydride mediates a number of free radical reductions and rearrangements. Also well known is the Stille reaction, the coupling of an organic group on tin with an organohalide or triflate in the presence of a palladium catalyst.[226] This reaction has been developed to the point of being catalytic in tin as well as palladium[227] and is widely used in organic synthesis. Carbon-

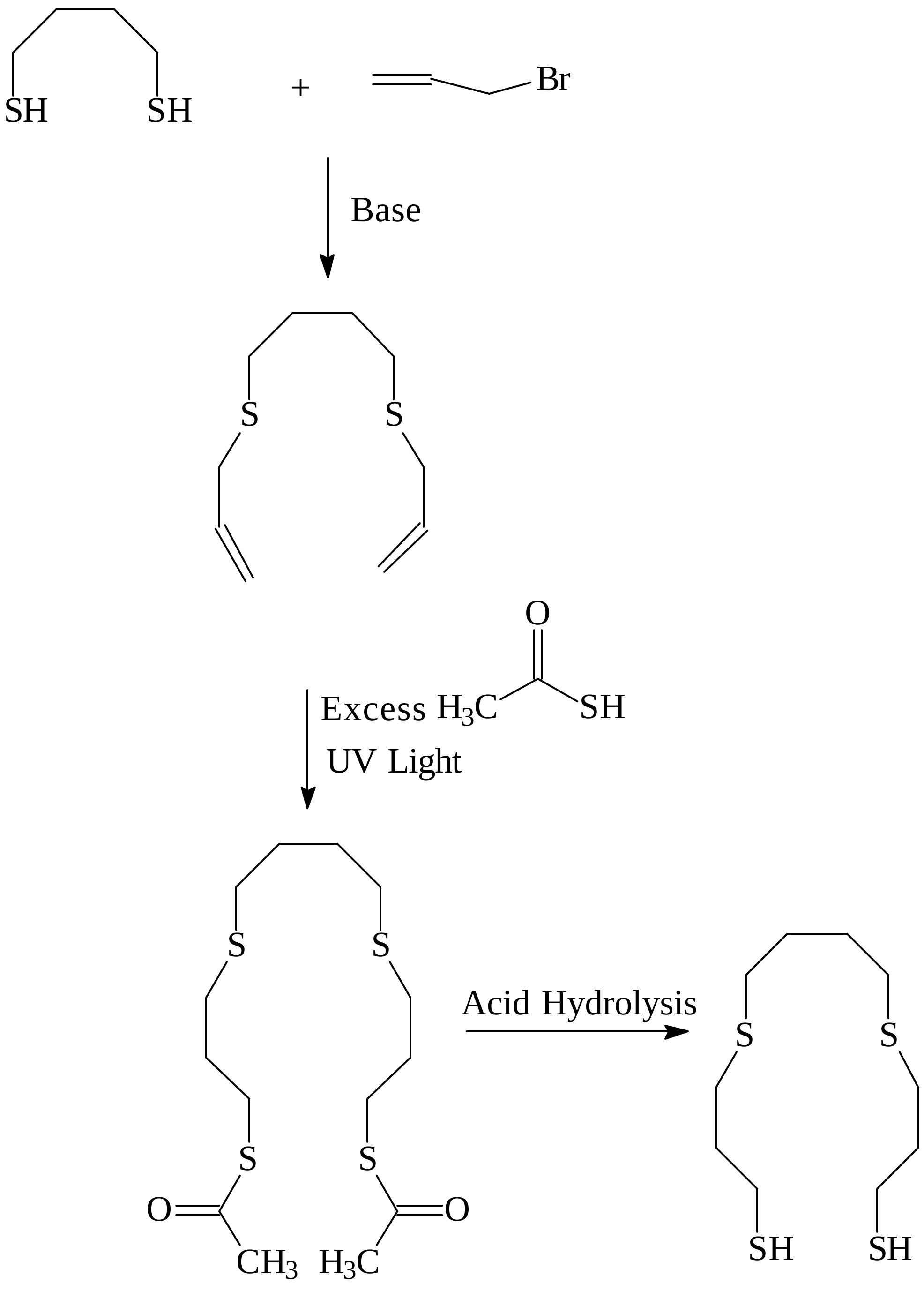


Figure 2.4: The diene route

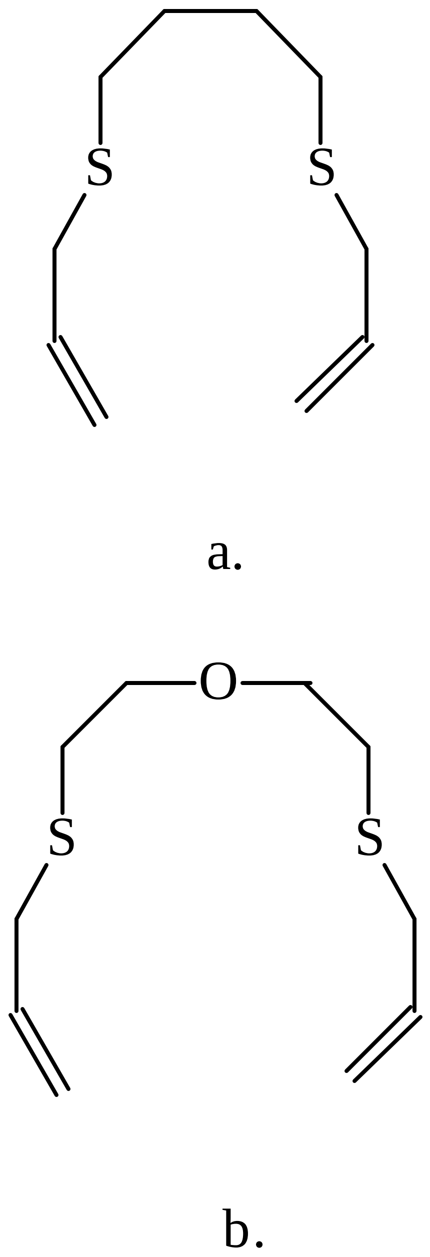


Figure 2.5: Some new dithioether dienes

tin bonds have also been found to add to a number of unsaturated compounds, including alkynes and dienes.[228] Alkenes and alkynes will add to tin hydrides in a free radical process known as hydrostannation.[229] Of particular interest for the author's purposes are the reactions of tin with allyl and sulfur species. The chemistry of tin with allyl groups is interesting and well studied. Tributylstannyllithium or tin (II) fluoride, when combined with diethylaluminum chloride, react with allyl phosphates to replace the phosphate with a tin species.[230] Tin (II) fluoride also inserts into the carbon-iodide bond of a trimethysilyl-substituted allyl iodide.[231] In the presence of a palladium catalyst, similar insertions occur for tin (II) chloride and allyl acetates[232] or allyl alcohols.[233] Tributyltin hydride, meanwhile, has been reported to cleave sulfur-carbon bonds in dithianes, resulting in addition of the thiols to the tin.[234] Therefore, it seemed likely that a compound with both allyl and sulfide functionality would form unique products with tin. Furthermore, if the resulting compound was soluble, it might provide an opportunity to obtain new ^{119}Sn NMR data.

To explore these possibilities, 2O2S3diene was combined with tin (II) chloride in diethyl ether (figure 2.6). After 24 hours of reflux, a white precipitate formed. The suspension was then filtered, and crystals suitable for X-ray analysis grew from the filtrate. These revealed a unique tin-thioether complex. The fact that this compound was recovered at all is quite interesting. Most of the previous work with tin (IV) halides had been performed under rigorous air-sensitive conditions due to the instability of these halides to atmospheric water. However, this comparable tin (II) complex was formed on the bench top, without any special effort being made to exclude water. Therefore, this complex appears to be somewhat more robust than its predecessors. However, if heated under vacuum or left open to the atmosphere for prolonged periods, it decomposes into a thick, yellow gel.

The X-ray structure (figure 2.7) reveals that the tin (II) atoms are in a five-coordinate pseudo-square pyramidal geometry gained through chloride bridging, not counting the secondary interaction suggested by the O-Sn distance of 2.887(4) Å. The bond length for the terminal chloride (2.467(2) Å) is comparable to that found in tin (IV) chloride thioether complexes, while the length of the bridging Cl-Sn(II) bond is, of course, slightly longer (2.759(2) Å). Although halide bridging is a motif not seen in similar tin (IV) thioethers, it has been found in other tin (II)[235] and tin (IV)[236] compounds. The square pyramidal geometry also appears to be new to tin-thioether chemistry, but not to tin chemistry in general.[237] Both sulfurs form bonds in the equatorial plane, along with the bridging chlorides. The terminal chloride is axial, with the apparently open axial coordination site occupied by a stereochemically active lone pair. The sum of the equatorial angles is 359.3(2)°, making them almost perfectly planar. The tin-sulfur bonds are longer than those in tin (IV) thioethers (approximately 3.031(1) Å vs. 2.6-2.7 Å[238-240]). This lengthening of the dative bond can be attributed to the greater electron density on a +2 center as opposed to +4 center. The tin-oxygen distance of 2.887(4) Å is well within the sum of Van der Waals radii (3.69 Å[241]), suggesting that there is, while perhaps not a true bond, a real interaction between these atoms. Including this interaction in the coordination sphere would put the tin in the rare pentagonal mono-pyramidal geometry.[242]

The complex is sparingly soluble in deutero-chloroform, permitting NMR studies to be performed. The ^{1}H and ^{13}C NMR of the complex and the decomposition product are identical to that of the free ligand, emphasizing the weakness of the donor-acceptor bonding in this system. The ^{119}Sn NMR of the complex showed a single, sharp peak at -125.8 ppm. There has been a wide range of ^{119}Sn chemical shifts reported for Sn(II). For example, Lappert has reported shifts from 766 ppm to -193 ppm for two-coordinate tin(II).[243] By comparison, the presumably five-coordinate species $SnCl_2 \cdot (THF)_x$ appears at -238 ppm.[244] Five-coordinate

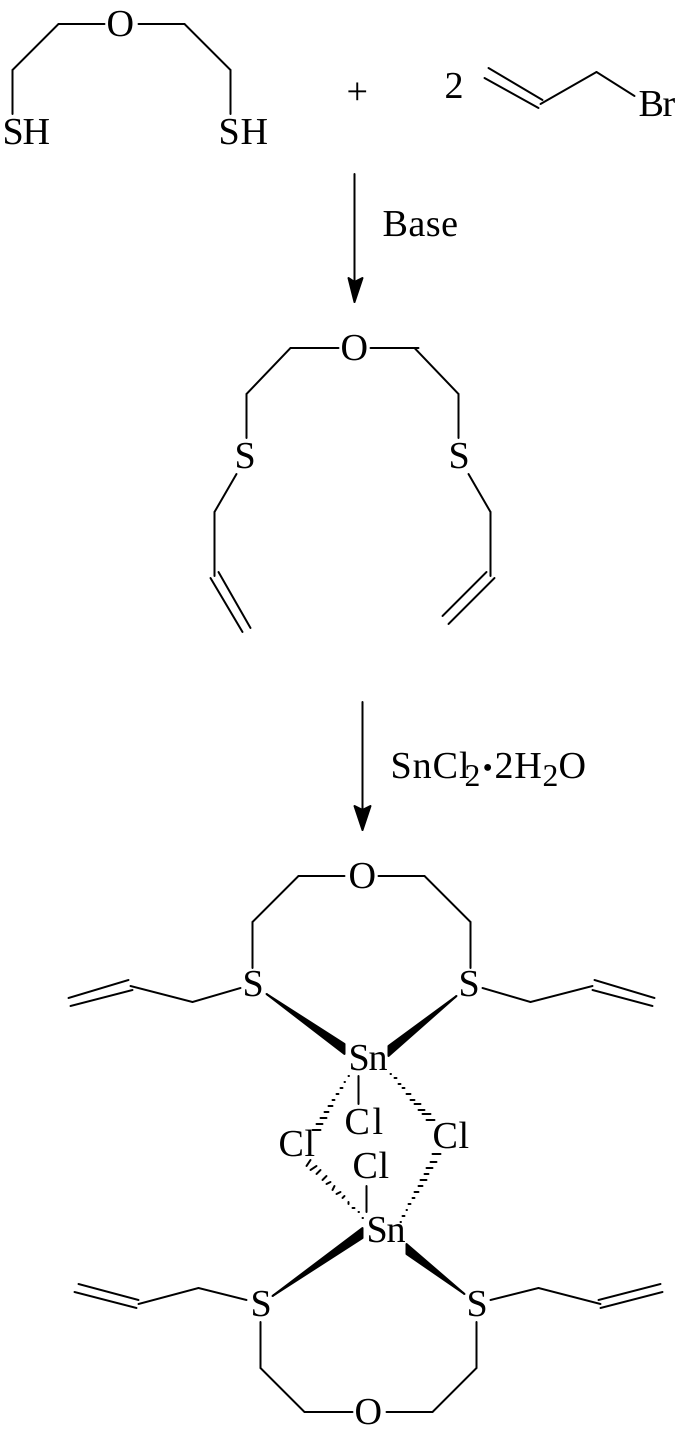


Figure 2.6: The reaction of 2O2S3diene and tin (II) chloride

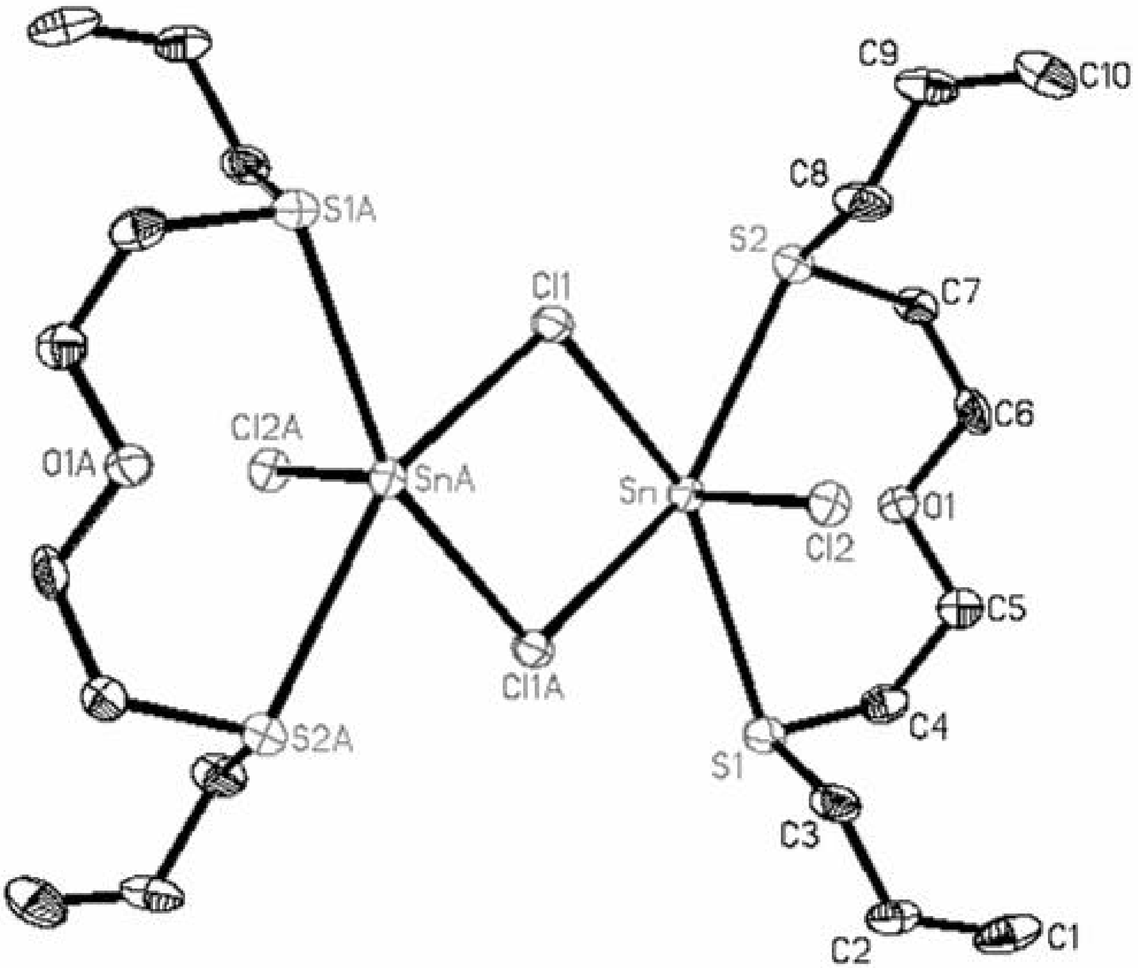


Figure 2.7: The tin dithioether diene dimer

organotin (IV) species with bridging chlorides have been reported at -221 ppm,[236] while other five-coordinate tin(IV) species were found to range from +25 ppm to -329 ppm[245] or from -27.0 ppm to -248.6 ppm.[246] A series of six-coordinate tin (IV) tetrachloride dithioethers were found to have shifts from -578 ppm to -560 ppm,[239] and a five-coordinate thioether could be expected to have shifts at significantly higher frequency than those. Therefore, -125.8 ppm does not appear unreasonable for a five-coordinate, chloride-containing Sn (II) thioether. The ^{119}Sn NMR of the yellow gel resulting from complex decomposition showed four sharp peaks at 900.0 ppm, 843.7 ppm, 702.5 ppm, and -859.4 ppm. This suggests that there are multiple Sn environments present after decomposition. It is worth noting that all but the peak at -843.7 ppm are outside the range expected for Sn (II) and probably represent 4- and 5-coordinate Sn (IV) species. This structure serves to demonstrate how new compounds, prepared during attempts to synthesize the targeted mercury binding agents, can be used in additional discovery-based research. Clearly more work could be done to explore the interaction of tin (II) species and dithioethers.

2.4 Alkyl Sulfide Ligands

Both the diol and diene compounds were made by combining reagents possessing a desired fuctional group and a halide separated by an alkyl chain with a dithiol. This is a technique that generally gave the desired compounds in good yields. Therefore, it appeared attractive to investigate whether the same technique could be adapted to make the dithioether dithiol target ligands. The basic problem with this is that an α-thiol-ω-haloalkane with three or four carbons would not be stable; these “arms” would be as likely to react with each other as with the dithiol “backbone”. Therefore, if this was to be a viable route to the target ligands, it would be necessary to place some group on the sulfur to prevent its reaction with the halide. There is literature precedent for this; Apparu used a similar method to make 3S2SH derivatives with benzyl groups initially protecting the terminal thiols.[222] However, he could not isolate α-thiol-ω-haloalkanes of greater than two carbons by this method. Therefore, a less easily removed group than benzyl was required for the current procedure; *tert*-butyl groups were ultimately chosen.

A clear starting point for this work would be to determine if any α-*tert*-butylthio-ω-haloalkanes have been synthesized before. A search of the literature reveals that such compounds are known. In particular, 4-chlorobutyl-*tert*-butyl sulfide ($Cl4S^tBu$) had been synthesized previously.[247] This was just one out of a large series of α-alkylthio-ω-haloalkanes Anklam made to demonstrate his new general route to the compounds. The synthesis was achieved by the dropwise addition of an alkylthiol and base solution to a dilute solution of dihalide. These reactions were run at room temperature to prevent cyclization; even so, the bromo and iodo variations of this compound readily cyclized to form *tert*-butyl-tetrahydrothiophenium halides (figure 2.8), which is why only 4- chlorobutyl-*tert*-butyl sulfide was isolated. Refluxing the solution only increases the rate of this reaction. Anklam found that yields were low, ranging from 17% to 50%.

The plan for this work was to use Anklam's procedure to create a sulfur-protected arm of the ligand, then combine that arm with dithiol to form a protected version of the target ligands, and finally remove the *tert*-butyl ligands to gain the desired thiol. Due to the greater stability of the three-carbon compounds, it was decided to primarily pursue 3-bromopropyl *tert*-butyl sulfide ($Br3S^tBu$) as the arm. This would yield an arm one carbon shorter than originally intended, but this version could be used to develop all the chemistry for this route and then be tested as a mercury precipitation agent. The results could then be compared with that of a ligand with four-carbon arms, made using the techniques developed while synthesizing the more readily available propyl arm variant (Figure 2.9).

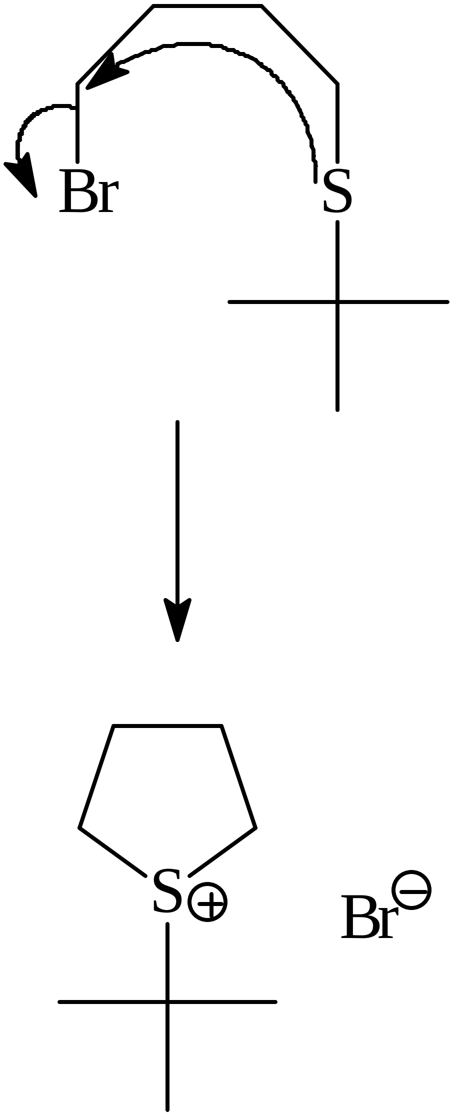


Figure 2.8: The cyclization of an “arm”

As a first step in this process, therefore, the synthesis of Br3S^{t}Bu was attempted. Sodium methoxide was produced in methanol (the lower boiling methanol proved easier to remove than ethanol without loss of the volatile product), then *tert*-butyl mercaptan was added and the solution stirred for roughly thirty minutes. The thiolate solution was then transferred to a dropping funnel and a second, concentrated solution of dibromopropane prepared. The dilute thiol solution was then added dropwise to dihalide and the resulting solution stirred at room temperature overnight. The reaction was worked up and the solvent was removed under vacuum, yielding the final product in approximately 30% yield. The corresponding 4-chlorobutyl *tert*-butyl sulfide was also synthesized, albeit in lower yield, presumably due to cyclization during the reaction. Little further work, beyond basic synthesis, has been done on this compound. Rather, most of the effort was devoted to perfecting the synthesis using the slightly more available three-carbon arm version.

Once these arms had been prepared, the next step was to combine them with a dithiol. Two equivalents of the new 3-bromopropyl *tert*-butyl sulfide (Br3S^{t}Bu) readily reacted with butanedithiol to yield a four-carbon backbone, three-carbon arm ligand with terminal *tert*-butyl sulfide groups: 2,2,17,17-tetramethyl-3,7,12,16-tetrathiaoctadecane (4S3S^{t}Bu). Initially, purification of this compound was somewhat difficult due to its high boiling point; during distillation more compound would be lost to decomposition than was recovered. However, the mixtures were eventually purified by column chromatography, using a 70% methylene chloride/30% hexane mixture. With some practice, it became possible to make over thirty grams of this compound at a time, with yields as high as 58%. Unfortunately, all efforts to remove the *tert*-butyl groups (whether by acid hydrolysis or reaction with sodium metal in liquid ammonia) resulted in either no reaction or decomposition of the compound.

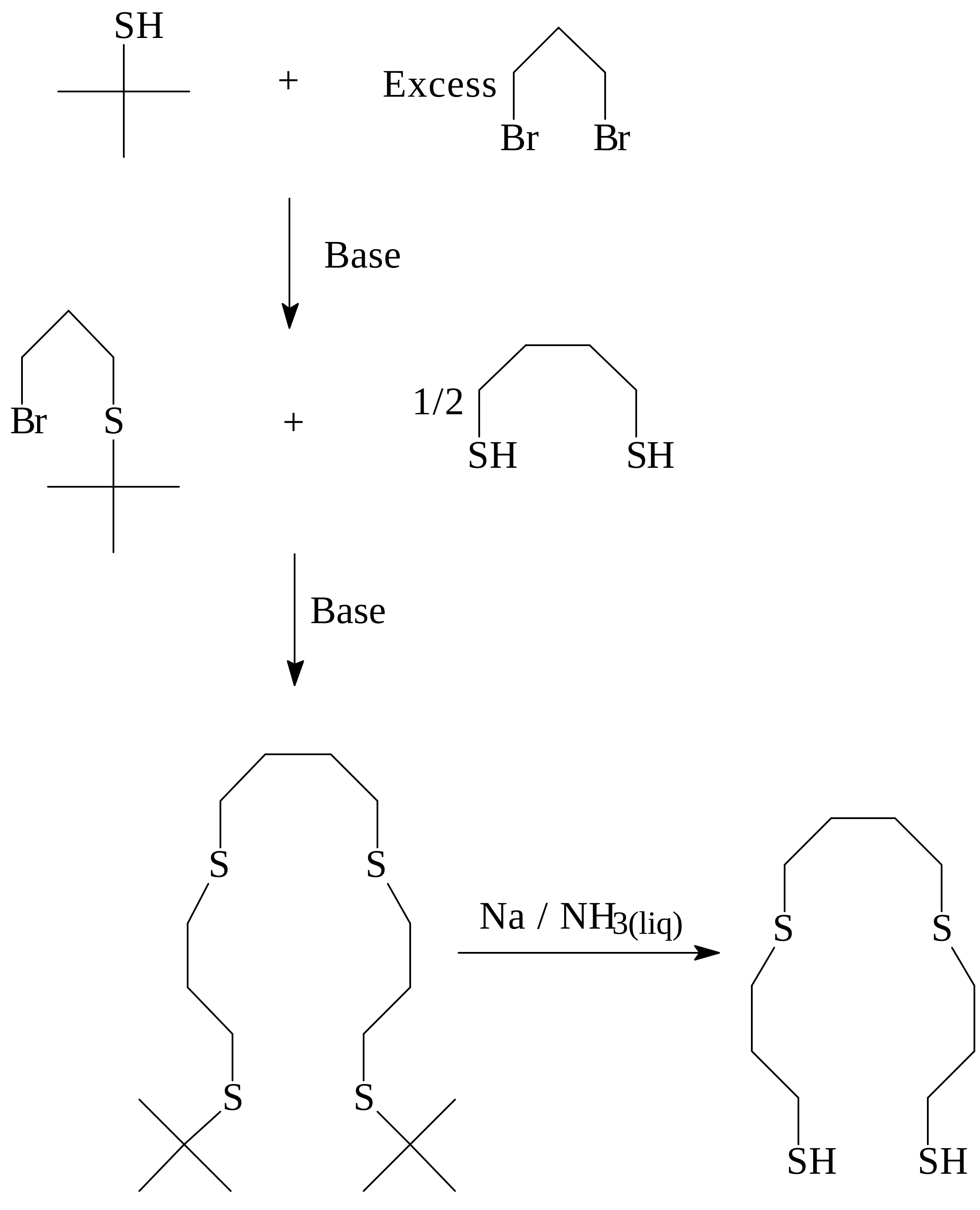


Figure 2.9: The *tert*-butyl route

With its four backbone sulfurs, this ligand is essentially an open chain variant of the sulfur macrocycles often used to bind mercury[158] and, in that light, a ligand of interest in its own right.[11, 202] Therefore, the ligand was combined with mercury (II) chloride in benzene, immediately resulting in the formation of a white precipitate. The heaviest recorded fragment in the mass spectrum of this precipitate showed the ligand associated with mercury chloride and an extra chloride atom. Elemental analysis, however, showed far less carbon, hydrogen, and sulfur than would be predicted for a simple complex with one ligand and one mercury chloride. The anlaysis did agree very well with one ligand and five mercury chlorides. The immediate question was whether this was the actual composition of the compound or if mercury chloride simply coprecipitated with a ligand-mercury complex. To determine this, the precipitate was washed in water and the elemental analysis was repeated. Mercury chloride is a water soluble compound and therefore it would be expected to be removed by washing if not associated with the ligand. The washing, however, led to only a very slight increase in the %C, H, and S. The new analysis fits well to a formula of one ligand to 4.3 mercury chloride. This indicates that the mercury chloride is in fact associated with the ligand, but it is not as strongly associated as it would be with a thiol ligand capable of forming essentially covalent bonds to the mercury.

One might wonder why this compound was not evaluated as a mercury precipitation agent itself. The reason is fairly simple. The main thrust of this work was the development of new chelates to precipitate mercury from water. Although not water soluble in their current, thiol, form, the 3S3SH, 3S4SH and 4S4SH ligands to be discussed in chapter three are candidates for this because they could be converted to group one metal thiolates and presumably made water soluble and therefore they were evaluated for use as mercury precipitators. This compound, on the other hand, has no thiol groups and therefore can not be converted to a water soluble thiolate, so it is not a candidate for precipitating mercury from polluted waters. It is a mercury chelator, however, and could conceivably have application in mercury sorbents if attached to a solid support, much like some of the other compounds reviewed in the mercury remediation section of Chapter one.[158]

Experimental Section

All reagents were purchased from Aldrich or Acros chemical companies and were reagent grade or better unless otherwise noted. All reactions involving trimethylaluminum or trimethylgallium were performed using strict air and moisture sensitive procedures (a glove box and Schlenk technique). NMR measurements were taken on a Varian Gemini 200 MHz NMR Spectrometer. IR spectroscopy was performed using either a Perkin Elmer model 1600 FT-IR spectrophotometer or a Nicolet Magna 560 FT-IR. Mass spectral data was gathered using either a JEOL JMS-700T magnetic sector instrument or a Shimadzu QP2010S instrument. Elemental analysis was performed by Galbraith Laboratories in Knoxville, TN. The percentage of carbon and hydrogen was determined by combustion according to the ASTM D5373 and D5291 methods. The percentage of sulfur was determined by combustion according to ASTM D4239 Method B and ASTM D1552. There was a ± 0.5% uncertainity in the measurements. Thermogravimetric analysis was performed by Edison Laboratories in Schenectady, NY, using a TA Instruments YGA2950, with a N_2 flow of 100 mL/min and a heating rate of 10° C/min. X-ray crystallography was performed by Sean Parkin at the University of Kentucky Crystallography using a Nonius kappaCCD instrument.

3S2OH: Sodium ethoxide (15.0 g, 220 mmol) was dissolved in approximately 200 mL of absolute ethanol, then 1,3-propanedithiol (1.00 mL, 109 mmol) was added. After this solution was stirred for a short time, 2-chloro-1-ethanol (15.0 mL, 224 mmol) was added and refluxed for two h. The solution was filtered and then the ethanol was removed via vacuum evaporation. Methylene chloride was added to precipitate excess salt, the mixture was filtered a second time, and the methylene chloride was also removed via vacuum pumping. The solution was distilled under vacuum (0.5 mm Hg), with the 3S2OH coming off at 170-195^{0}C. Yield: 12.0g (61.2 mmol), 56%, ^{1}H NMR (CDCl$_3$, 200 MHz,): d 3.75 (t, 4H), 2.91 (s, 2H), 2.68 (m, 8H), 1.89 (p, 2H), ^{13}C NMR (CDCl$_3$, 200 MHz): d 60.7, 34.7, 30.4, 29.2, IR (thin film on NaCl plates, cm^{-1}): 3300(s, b), 2918(s), 1640(w), 1420(s), 1340(m), 1290(s), 1260(s), 1226(m), 1164(m), 1044(s), 1010(s), 942(m), 824(m), 762(m), 586(m), 534(m), 522(m), GC-MS**:** Peak at RT = 4.52 min, *m/z* = 196 (M$^+$), purity by GC: 99.5%.

3S2SH: 3S2OH (4.00 g, 20.4 mmol) was combined with thiourea (3.32 g, 43.6 mmol) in 10 mL concentrated HCl. The resulting solution was refluxed for 10 h. Then potassium hydroxide (6.90 g, 123 mmol) in 40 mL of DI water was slowly added, and the solution refluxed for 3 h. The resulting two-phase system was separated, and the upper, aqueous phase was extracted with ether. The ether was added to the organic layer and the resulting mixture was distilled between 159-161°C at 0.5 mm Hg to yield 3S2SH. Yield: 2.5 g (11.0 mmol), 54%, ^{1}H NMR (CDCl$_3$, 200 MHz): d 2.75 (m, 8H), 2.64 (t, 4H), 1.87 (p, 2H), 1.73 (t, 2H), ^{13}C NMR (CDCl$_3$, 200 MHz): d 36.1, 30.6, 29.3, 24.7, IR (thin film on NaCl plates, cm^{-1}): 2914(s), 2842(m), 2544(m), 1608(w), 1428(s), 1342(m), 1272(s), 1256(s), 1210(s), 1140(m), 964(m), 888(w), 848(m), 770(m), 698(s), 518(w), GC-MS: Peak at RT = 5.43 min, *m/z* = 228 (M$^+$), purity by GC: 97.6%.

3S4OH: Sodium metal (3.39 g, 147 mmol) was dissolved in approximately 150 mL of absolute ethanol. To this was added 1,3-propanedithiol (7.40 mL, 73.0 mmol), and the solution was permitted to stir for approximately 30 min. 4-Chloro-1-butanol (14.7 mL, 147 mmol) was then added, and the solution was refluxed for 3 h. After reflux, the ethanol was stripped off via vacuum evaporation, acidified with dilute HCl, and extracted in methylene chloride. The methylene chloride layer was distilled between 166-184°C at 0.4 mm Hg to yield the desired product. Yield: 7.64 g (30.3 mmol), 41%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 3.7 (m, 4H), 2.79 (s, 2H), 2.59 (m, 8H), 1.86 (q, 4H), 1.65 (m, 8H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 62.1, 31.9, 31.8, 30.8, 29.4, 26.00, IR (thin film on NaCl plates, cm^{-1}): 3382 (br, s), 2935 (s), 2863 (m), 1667 (w), 1474 (m), 1437 (m), 1384 (w), 1296 (w), 1261 (m), 1060 (s), 803 (m); GC-MS: peak at RT= 6.43min, *m/z* = 252 (M^+), purity by GC: 93.0%.

4S2OH (method 1): Sodium metal (4.41 g, 192 mmol) was dissolved in approximately 150 mL of absolute ethanol. To this solution was added 1,4-butanedithiol (90% tech grade, 10.0 mL, 76.7 mmol), and the solution was stirred for approximately 30 min. Then 2-chloroethanol (15.4 mL, 230 mmol) was added and the solution was refluxed for 3 h. The ethanol was removed by vacuum evaporation, acidified, and extracted with diethyl ether. The ether layer was distilled between 150-152°C at 0.4 mm Hg to yield the pure product. Yield: 11.8g (56.2 mmol), 73%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 3.74 (t, 4H), 3.01 (s, 2H), 2.72 (t, 4H), 2.55 (t, 4H), 1.71 (m, 4H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 60.6, 35.3, 31.4, 28.7, IR (thin film on NaCl plates, cm^{-1}): 3358 (br, s), 2918 (s), 2863 (s), 1642 (m), 1458 (s), 1412 (s), 1356 (m), 1314 (m), 1288 (m), 1228 (m), 1198 (m), 1162 (m), 1040 (s), 1007 (s), 770 (w), 720 (w), 636 (w), GC-MS: peak at RT= 16.24 min., *m/z* =210 (M^+), purity by GC: 98.4%.

4S2OH (method 2): Sodium metal (6.01 g, 261 mmol) was dissolved in approximately 200 mL of absolute ethanol. To this solution was added 2-mercaptoethanol (17.6 mL, 251 mmol). The solution was stirred for approximately 30 min, then 1,4-dibromobutane (12.0 mL, 100 mmol) was added, and the solution was refluxed for 3 h. After reflux, the ethanol was removed via vacuum evaporation and the residue was acidified, then extracted with diethyl ether.

The ether layer was distilled between 150-152°C at 0.4 mm Hg to yield the pure product.. Yield**:** 11.7 g (55.7 mmol), 56%, ^{1}H NMR (CDCl$_3$, 200 MHz): d 3.74 (t, 4H), 3.01 (s, 2H), 2.72 (t, 4H), 2.55 (t, 4H), 1.71 (m, 4H), ^{13}C NMR (CDCl$_3$, 200 MHz): d 60.6, 35.3, 31.4, 28.7, IR (thin film on NaCl plates, cm^{-1}): 3358 (br, s), 2918 (s), 2863 (s), 1642 (m), 1458 (s), 1412 (s), 1356 (m), 1314 (m), 1288 (m), 1228 (m), 1198 (m), 1162 (m), 1040 (s), 1007 (s), 770 (w), 720 (w), 636 (w), GC-MS: peak at RT= 16.24 min., *m/z* =210 (M$^+$), purity by GC: 98.4%.

4S2-*tert*-OH: Sodium metal (1.37 g, 59.6 mmol) was dissolved in approximately 60 mL of absolute ethanol. To this solution was added 1,4-butanedithiol (2.70 mL, 23.2 mmol), followed by 30 min stirring, then the addition of chloro-*tert*-butanol (6.00 mL, 58 mmol). The solution was refluxed for 3 hours, then the ethanol removed via vacuum. The residue was acidified and extracted with methylene chloride. The methylene chloride layer was distilled between 138-139°C at 0.4 mm Hg to yield the product. Yield: 3.90 g (14.7 mmol), 63%, ^{1}H NMR (CDCl$_3$, 200 MHz): d 3.20 (s, 2H), 2.65 (s, 4H), 2.58 (m, 4H), 1.69 (m, 4H), 1.25 (s, 12H), ^{13}C NMR (CDCl$_3$, 200 MHz): d 70.5, 46.7, 33.9, 28.8, 28.6, IR (thin film on NaCl plates, cm^{-1}): 3406 (br, s), 2970 (s), 2930 (s), 2860 (m), 1638 (w), 1458 (m), 1372 (s), 1312 (w), 1214 (m), 1146 (s), 1050(s), 964 (m), 906 (m), 858 (m), 726 (w); GC-MS: peak at RT= 18.06 min, *m/z* = 266 (M$^+$), purity by GC: 93.9%.

4S3OH: Sodium hydroxide (6.94 g, 174 mmol) was dissolved in 250 mL of absolute ethanol. To this solution was added 1,4-butanedithiol (10.0 mL, 86.7 mmol) followed by 30 minutes stirring, then the addition of 3-chloro-1-propanol (16.4 mL, 195.7 mmol). The solution immediately became white and cloudy. The solution was refluxed for 3 hours, then the ethanol removed via vacuum. The residue was acidified and extracted with methylene chloride, which was then distilled between 168-169°C at 0.4 mm Hg to yield the product. Yield: 18.3 g (76.8 mmol), 89%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 3.73 (t, 4H), 3.25 (s, 2H), 2.63 (t, 4H), 2.50 (t, 4H), 2.25 (m, 4H), 1.69 (m, 4H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 61.2, 33.9, 32.1, 28.6, 28.5, IR (thin film on NaCl plates, cm^{-1}): 3365 (br,s), 2924 (s), 2859 (m), 1700 (m), 1635 (m), 1428 (s), 1352 (m), 1276 (w), 1259 (w), 1148 (m), 1048 (s), 903 (m), 872 (w), 714 (w), GC-MS: peak at RT= 6.43 min, *m/z* = 238 (M^+), purity by GC: 98.8%.

4S2-*tert*-OH with $AlMe_3$: The 4S2-*tert*-OH ligand (5.30 g, 27.4 mmol) was dissolved in 130 mL dry toluene, then trimethylaluminum (1.98 g, 27.4 mmol) in 10 mL toluene was added dropwise. The immediate evolution of gas was observed. After one hour reflux, the solvent was concentrated by vacuum and the translucent solid product isolated by filtration. Yield: 4.8g (15.7 mmol), 57%, IR (KBr Pellet, cm^{-1}): 2968 (s), 2953 (s), 2895 (w), 1612 (w), 14.88 (m), 1456 (m), 1370 (m), 1217 (w), 1195 (m), 1164 (m), 1130 (s), 1045 (m), 980 (w), 689 (s), Mass Spectrum: a number of fragments, including *m/z* = 143 ($Al(OC(CH_3)_2)_2$), *m/z* = 231 ($(CH_3)AlOC(CH_3)_2CH_2SCH_2CH_2CH_2CH_2S$), *m/z* = 249 ($(CH_3)Al(OC(CH_3)_2CH_2S)_2$); Anal. for 4S2-*tert*-$OAlCH_3$, Calcd. (Found): C 50.95% (50.13%), H 8.88% (9.09%), S 20.93% (21.10%).

4S3diene: Sodium metal (1.50 g, 65.2 mmol) was dissolved in approximately 150 mL of absolute ethanol. To this solution was added 1,4-butanedithiol (3.00 mL, 25.0 mmol) and the solution was stirred for approximately 30 min. Then allyl bromide (4.50 mL, 51.0 mmol) was added. The solution was immediately filled with a white precipitate. It was refluxed for 2 h, then the ethanol removed via vacuum evaporation. The white residue was acidified, then extracted with ether, and the ether layer distilled between 80-83°C at 0.4 mm Hg, yielding the desired product. Yield: 4.30 g (21.3 mmol), 85%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 5.71 (m, 2H), 5.09 (d, 2H), 4.98 (s, 2H), 3.05 (d, 4H), 2.49 (m, 4H), 1.59 (m, 4H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 134.5, 116.3, 34.5, 29.9, 27.9, IR (thin film on NaCl plates, cm^{-1}): 3078 (s), 3006 (w), 2974 (m), 2912 (s), 2850 (m), 1825 (m), 1634 (s), 1426 (s), 1402 (m), 1358 (w), 1282 (m), 1226 (s), 1118 (w), 1080 (w), 988 (s), 916 (s), 880 (w), 746 (m), GC-MS: peak at RT= 11.38 min, *m/z* = 161 (M$^+$ minus one allyl group, M$^+$ not seen for these molecules), purity by GC: 100%.

2O2S3diene: Sodium metal (1.40 g, 60.9 mmol) was dissolved in absolute ethanol. To this solution was added 2-mercaptoethyl ether (4.0 mL, 31.0 mmol), followed by 30 min of stirring. Then allyl bromide (5.30 mL, 61.0 mmol) was added and a white suspension immediately formed. This was refluxed for 3 h, then the ethanol was removed under vacuum, the residue acidified with dilute hydrochloric acid, and extracted with methylene chloride. The methylene chloride layer was distilled between 143-150°C at 0.4 mm Hg, yielding the desired product. Yield: 5.80 g (26.6 mmol), 86%. ^{1}H NMR ($CDCl_3$, 200 MHz): d 5.79 (m, 2H), 5.15 (d, 2H), 5.05 (s, 2H), 3.61 (t, 4H), 3.15 (d, 4H), 2.64 (t, 4H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 134.3, 116.6, 70.6, 35.0, 29.6, IR (thin film on NaCl plates, cm^{-1}): 3078 (m), 3006 (w), 2914(s), 2858(s), 2788(w), 1840(w), 1634(m), 1460(w), 1426(s), 1404(m), 1356(m), 1292(m), 1226(m), 1112(s), 1036(w), 1020(m), 990(s), 916(s), 868(w), 746(m), GC-MS: peak at RT=14.30 min., *m/z* =177 (M$^+$ minus one allyl), purity by GC: 97.8%.

2O2S3diene-SnCl$_2$ Complex: Tin (II) chloride dihydrate (1.0 g, 4.42 mmol) was dissolved in diethyl ether. To this was added 2O2S3diene (0.97 g, 4.45 mmol) and the solution was refluxed for 24 h. During the course of the reflux, a white precipitate, identified as the complex by NMR, formed. The suspension was filtered and the filtrate placed in a freezer at -30^{0}C, where non-merohedrally twinned crystals eventually formed. Yield: 1.0 g (2.45 mmol), 55%, ^{1}H NMR (CDCl$_3$, 200 MHz): d 2.65 (t, 2H), 3.15 (d, 2H), 3.60 (t, 2H), 5.11 (m, 2H), 5.75 (m, 1H), ^{13}C NMR (CDCl$_3$, 200 MHz): d 134.3, 117.1, 70.4, 35.0, 29.9, ^{119}Sn NMR(CDCl$_3$, 200 MHz): d -125.8, IR (thin film on NaCl plates, cm^{-1}): 3074(m), 3001(m), 2970(s), 2947(m), 2866(s), 2794(w), 2701(w), 1844(m), 1632(s), 1462(s), 1426(s), 1406(s), 1360(s), 1302(s), 1226(s), 1210(m), 1196(m), 1100 (s), 1014(s), 986(s), 920(s), 866(m), 766(m) 742(m).

4S3S^{t}Bu: Sodium metal (1.20 g, 52.2 mmol) was dissolved in approximately 100 mL of anhydrous methanol. To this was added *tert*-butyl thiol (6.00 mL, 53.0 mmol) and the solution was allowed to stir for 30 min then transferred to a dropping funnel. The flask was washed with a 50 mL aliquot of anhydrous methanol, which was also added to the dropping funnel. 1,3-Dibromopropane (10.8 mL, 106 mmol) was added to the flask, along with 70 mL of anhydrous methanol. The thiol solution was then added dropwise to the dihalide solution. The combined solutions were allowed to stir for approximately 12 h, then the methanol was removed under vacuum. The residue was acidified with dilute hydrochloric acid, extracted with methylene chloride, and the methylene chloride removed under vacuum. The remaining clear liquid was set aside. In a separate flask, sodium metal (0.430 g, 18.7 mmol) was dissolved in 100 mL of absolute ethanol. To this solution was added butanedithiol (0.950 mL, 8.10 mmol), and it was stirred for 30 min. Then the clear liquid resulting from the reaction of the *tert*-butyl thiol and the 1,3-dibromopropane (3-bromopropyl-*tert*-butyl sulfide, 3.40g, 16.1 mmol) was added. The solution soon became white and cloudy. It was refluxed for 3 h, and then the ethanol removed under vacuum, the residue acidified with dilute hydrochloric acid, and the mixture extracted with methylene chloride. The methylene chloride layer was concentrated by evaporation, then run through a silica gel column (using a mixture of 70% methylene chloride/ 30% hexane as the mobile phase) to isolate the desired product. Yield: 1.80 g (5.11 mmol), 63%, ^{1}H NMR

($CDCl_3$, 200 MHz): d 2.62 (t, 2H), 2.60 (t, 2H), 2.53 (t, 2H), 1.84 (m, 2H), 1.69 (m, 2H), 1.32 (s, 9H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 42.2, 31.7, 31.4, 31.1, 29.8, 28.8, 27.3, IR (thin film on NaCl plates, cm^{-1}): 2942 (s), 2860 (s), 1458 (s), 1390 (w), 1362 (s), 1296 (m), 1258 (m), 1164 (s), 1124 (w), 850 (w), GC-MS: peak at RT= 25.53 min, *m/z* = 382, purity by GC: 95.8%.

$4S3S^tBu(HgCl_2)_5$: Mercury chloride (0.711 g, 2.62 mmol) was dissolved in 100 mL of benzene. The $4S3S^tBu$ ligand (1.00 g, 2.62 mmol) was then added to the solution. A white precipitate immeadiately formed. The precipitate was isolated by filtration and identified as $4S3S^tBuHgCl_2$. Yield: 0.486 g (0.279 mmol), 53%, IR (KBr Pellet, cm^{-1}): 2966 (s), 2916 (s), 2852 (m), 1616 (m), 1480 (w), 1416 (m), 1364 (m), 1246 (w), 1158 (s), 1108 (w), 854 (w), Mass Spectrum: Highest peak *m/z* = 691 ($4S3S^tBuHgCl_3$), TGA: one mass loss from 75°C-90°C of 2.50%, one mass loss from 110-152°C of 6.60% , one mass loss from 152°C-265°C of 56.77%, one mass loss from 260°C-380°C of 32.01%, Anal. for $4S3S^tBu(HgCl_2)_5$, Calcd. (Found): C 12.42% (12.77%), H 2.09% (2.10%), S 7.37% (7.14%). Some of the precipitate (0.15 g) was further washed with 50 mL of DI water. Anal for $4S3S^tBu(HgCl_2)_{4.3}$, Calcd. (Found): C 13.95% (14.32%), H 2.34% (2.24%), S 8.27% (8.06%).

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Chapter Three: Synthesis and Application of the Thiol Ligands

3.1 The Synthesis of 3S4SH and 4S4SH

The simplest approach for the synthesis of ligands such as 3S4SH and 4S4SH would be to perform a double S_N2 substitution with two dithiols and a dihalide. The very well-known S_N2 mechanism involves a nucleophile attacking the σ^* orbital of a carbon-halide bond.[248] This results in the nucleophile replacing the halide on carbon, with consequent inversion of stereochemical configuration. If a dithiol was deprotonated by a base and then exposed to a α,ω-dihalide, one end of two different dithiols could act as nucleophiles and attack each halide resulting in ligands of the desired form (figure 3.1), along with several other potential products. As the scheme shows, this reaction holds a significant likelihood of producing multiple side products. A 1:1 or 2:2 reaction of dithiol with dihalide would yield a macrocycle. Also, once one end of a dithiol has coordinated, the other dithiol sulfur could attack a completely separate molecule of dihalide, potentially creating ligands with arms of widely varying length. Some steps were taken, however, to suppress these side reactions. First, a large excess of dithiol and base were used. These were added to the reaction vessel first, followed by the dihalide. The dihalide was then added slowly, so as to ensure that each molecule of dihalide saw a large excess of dithiol. It was hoped that this would ensure that each halide combined with a fresh dithiol molecule, rather than an intramolecular reaction occurring to form a macrocycle.

Initially, several efforts were made to perform this reaction using sodium salts (sodium ethoxide, sodium *tert*-butoxide, and sodium hydride) as the base, with a variety of solvents and various periods of reflux used. However, these efforts did not yield any appreciable amounts of

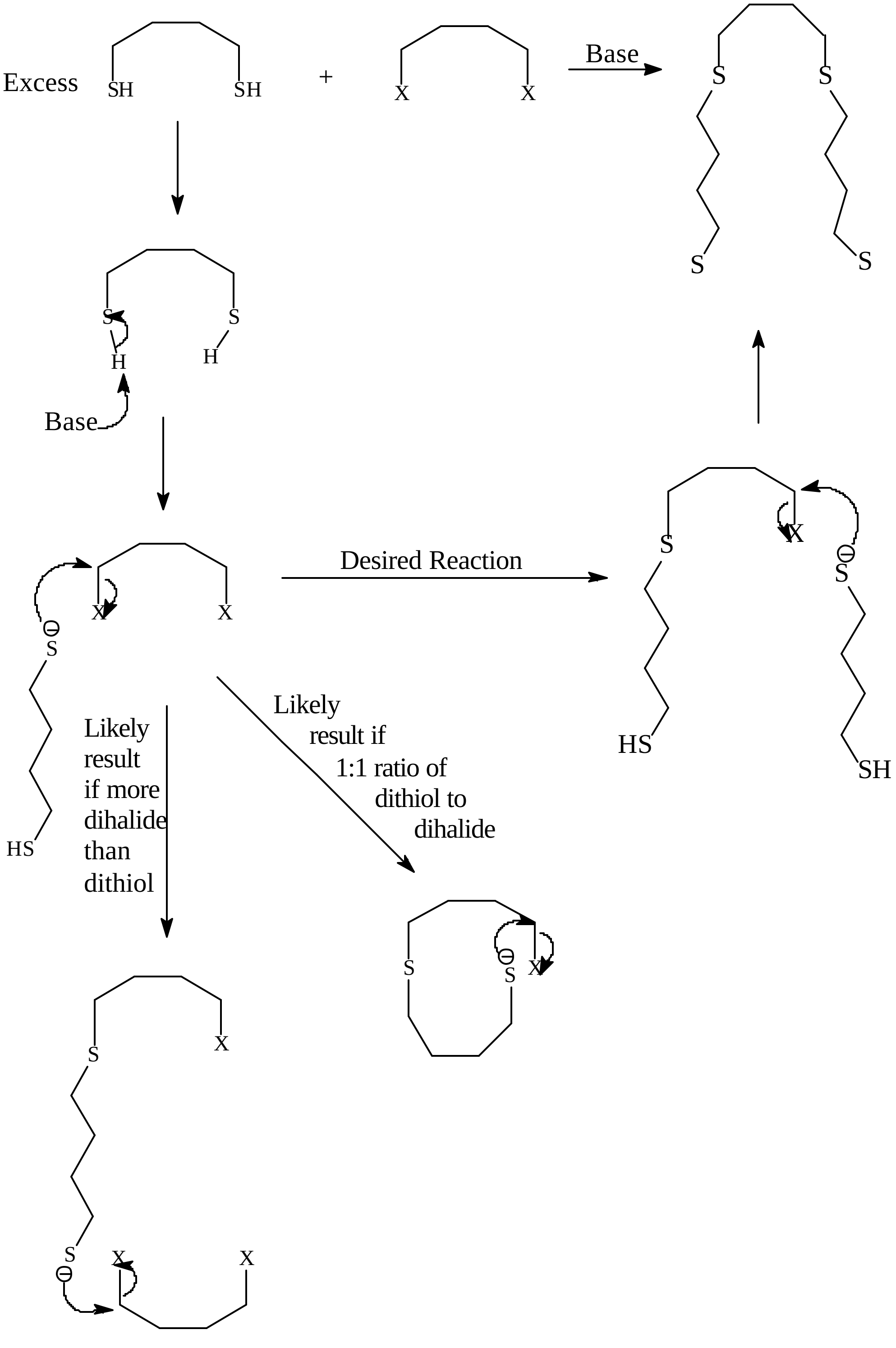
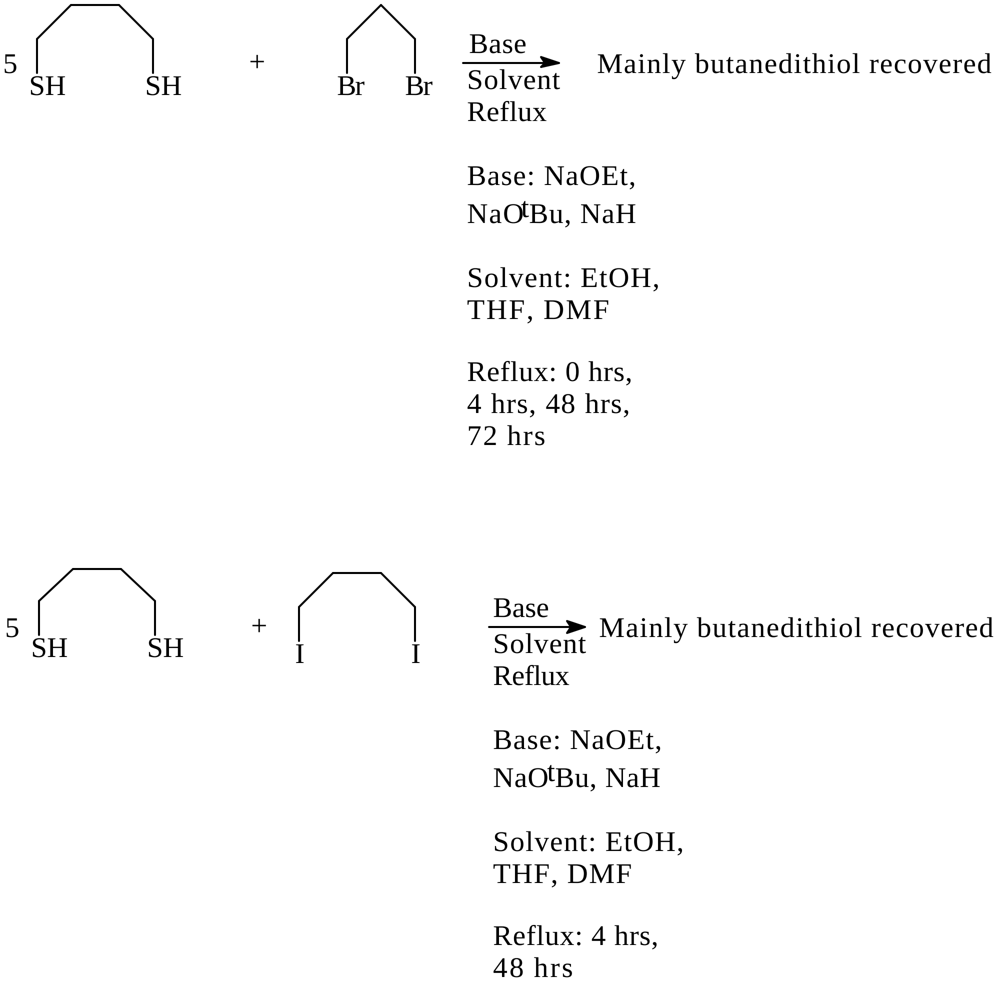


Figure 3.1: Direct halide substitution plan

the desired product (figure 3.2). This can be explained by referencing Ochrymowycz's painstaking study of thiacrown ether synthesis, during which he noted an interesting side reaction.[249] He observed interchain cyclization during the reaction of dithiols with dihalides, which proceeded through a sulfonium intermediate that replaced the halide as the leaving group for an S_N2 attack (figure 3.3). It is not hard to picture a similar reaction occurring in the present system. The first step would involve the expected attack by a thiolate on one end of the dihalide. However, the sulfide linkage could then use one of its lone pairs to attack the other halide, forming a cyclic thietane or tetrahydrothiophene derivative. These are themselves decent leaving groups and it is now possible for the other end of the dithiol to swing around and cyclize itself, resulting in the net production of two cyclic thiols from one molecule of dithiol and one of dihalide (figure 3.4). Both of these compounds are low enough boiling that they could be conceivably evaporate when the solvent is stripped from the reaction. This would explain why time after time only butanedithiol was recovered from the reactions.

Literature reports suggested that S_N2 substitutions involving dithiols and dihalides tended to occur in significantly better yields when Cs_2CO_3 is used as the base (figure 3.5).[250] It is assumed that this is due to the large size of the cesium cation (at 169 pm possibly the largest common cation[251]), which leads one to consider the sulfur cesium bond to be especially ionic and therefore a cesium thiolate especially nucleophilic.[3] Because the cesium thiolates were more nucleophilic than the sodium thiolates, they reacted more rapidly. Therefore, the rate of halide displacement by metal thiolate is increased compared to the rate of cyclization, resulting in a better yield of the desired product.

Due to the high cost of cesium salts, it would be desirable to avoid their use in this carbon arms. However, other methods had proved unseccesful. Therefore, a cesium- based sulfur



Mainly butanedithiol recovered

Base: NaOEt,
NaO^{t}Bu, NaH

Solvent: EtOH,
THF, DMF

Reflux: 0 hrs,
4 hrs, 48 hrs,
72 hrs

Mainly butanedithiol recovered

Base: NaOEt,
NaO^{t}Bu, NaH

Solvent: EtOH,
THF, DMF

Reflux: 4 hrs,
48 hrs

Figure 3.2: Summary of direct substitution reactions attempted

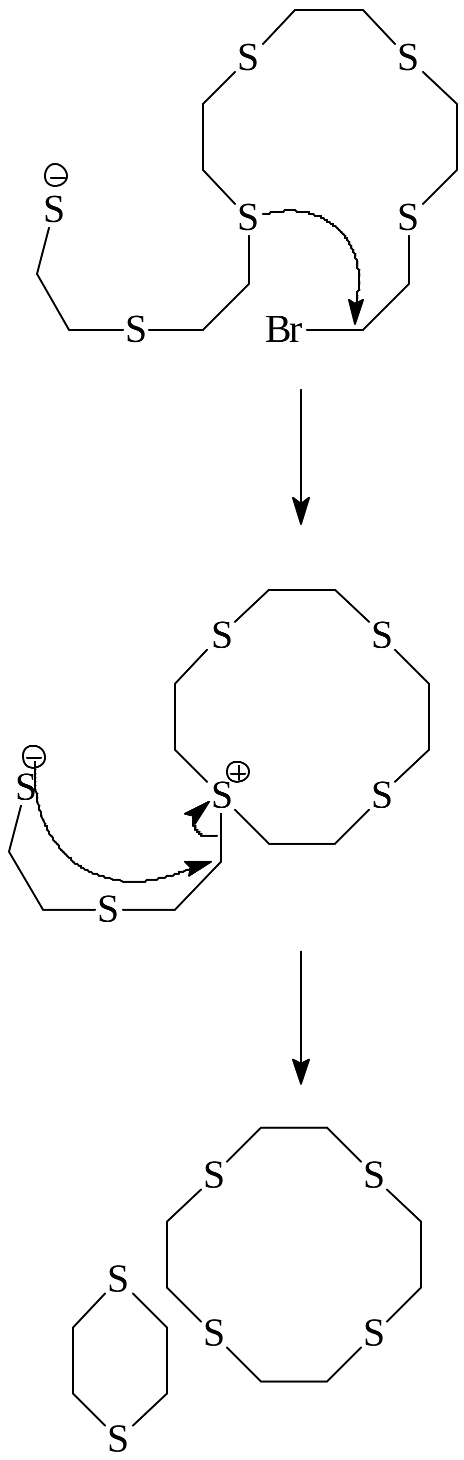


Figure 3.3: Results of Ochrymowycz's study of crown thioether synthesis

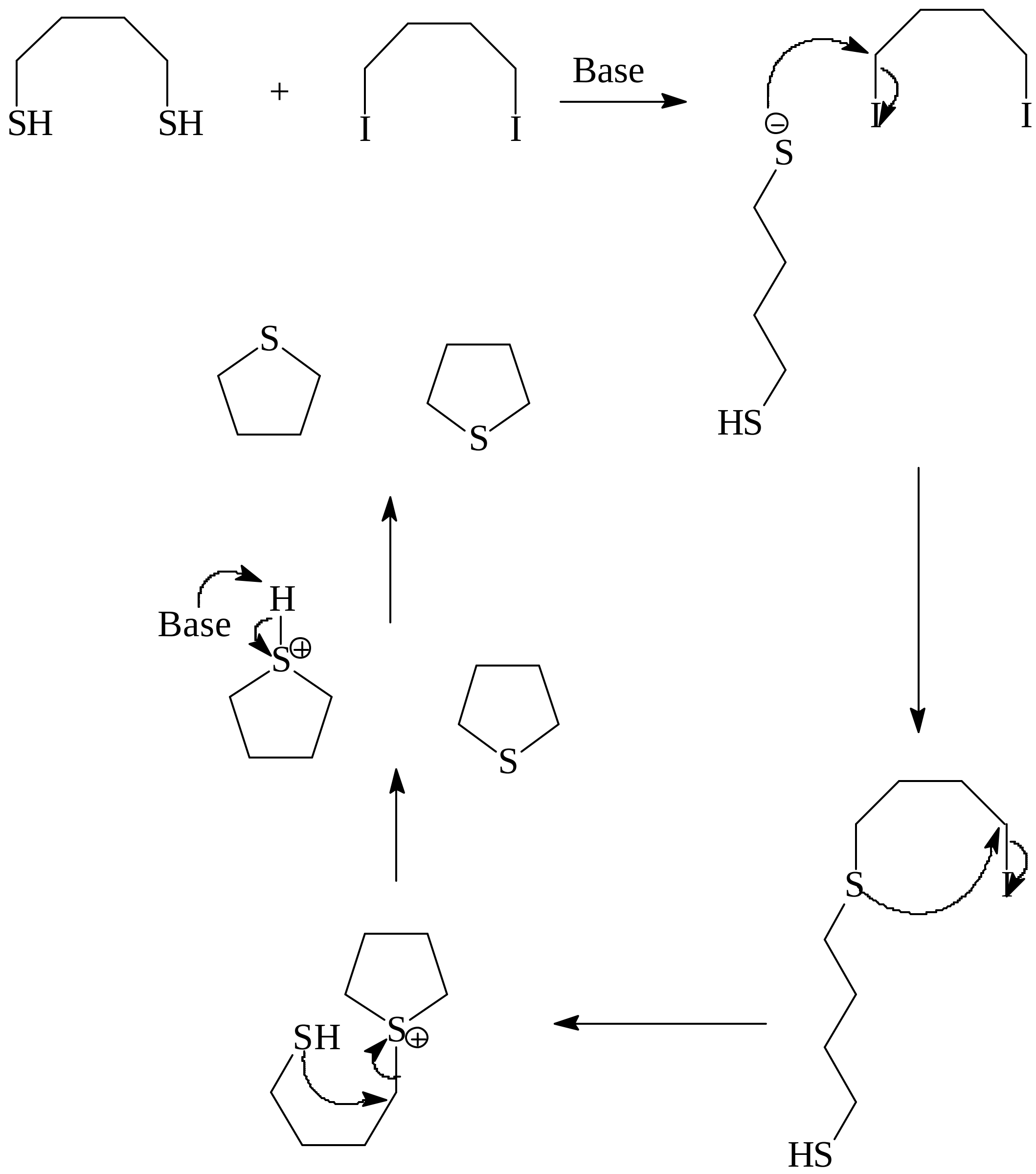


Figure 3.4: Possible mechanism for the failure of the sodium salt S_N2 reactions

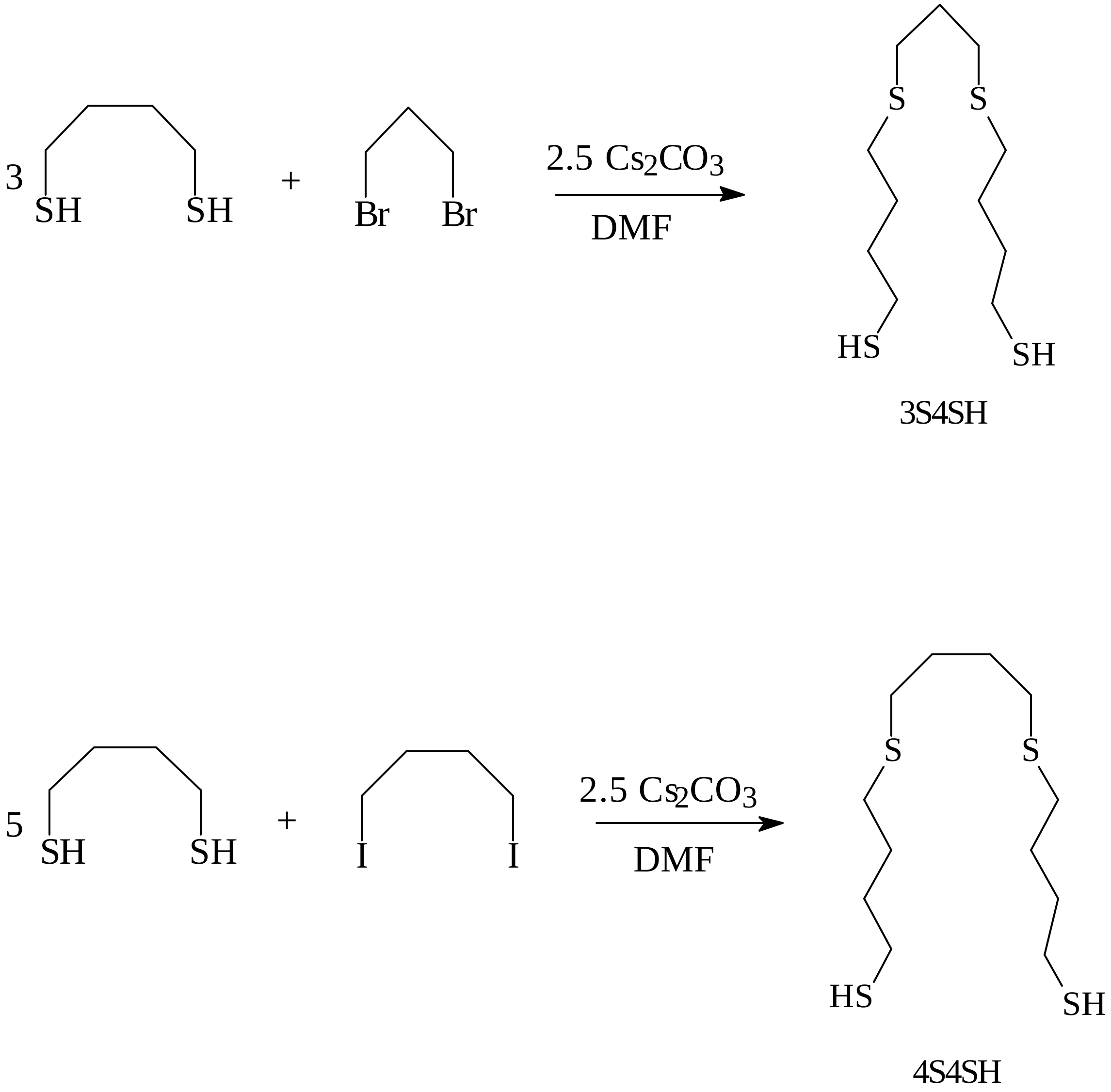


Figure 3.5: The cesium route

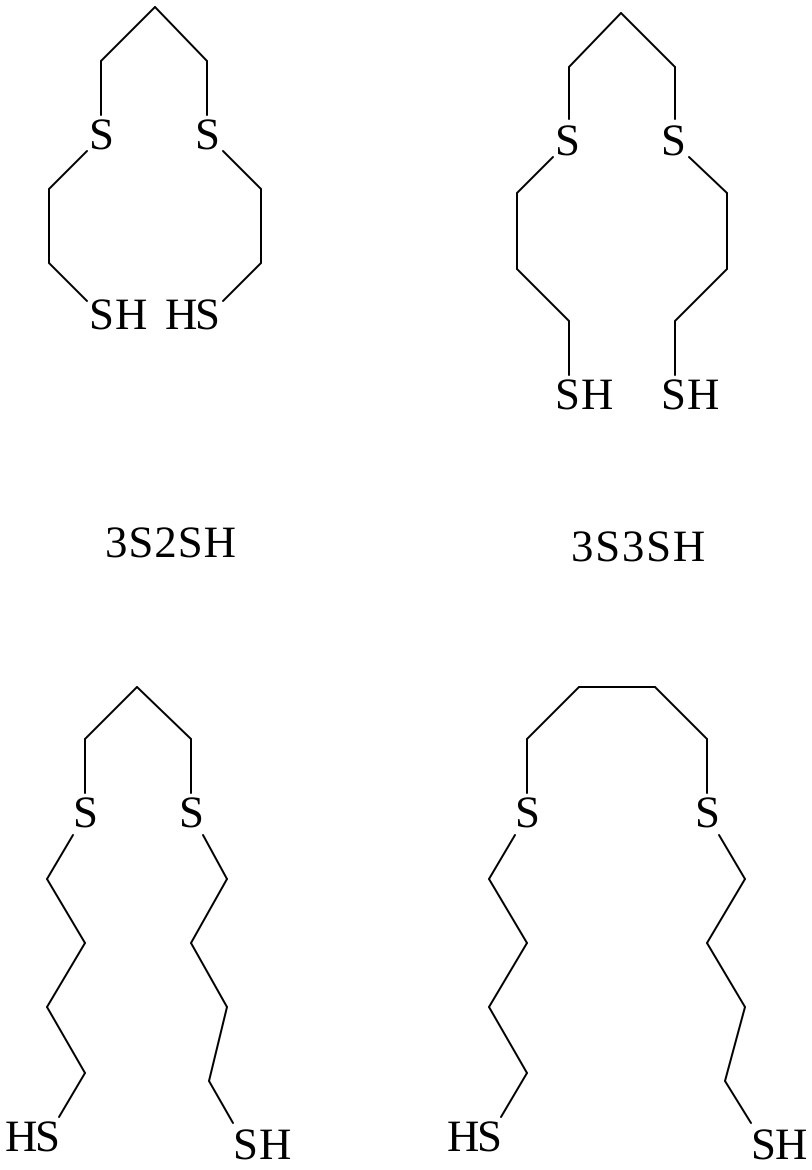
macrocycle synthesis reported in the literature[250] was adapted for making ligands such as 4S4SH and 3S3SH.

To test if this adapted synthesis would work, three equivalents of butanedithiol were combined with two and a half equivalents of cesium carbonate in DMF. This formed a suspension that was allowed to stir for thirty minutes. Then one equivalent of diiodobutane was slowly added and the mixture left to stir for at least twenty-four hours. Afterwards, the DMF was distilled off, the residue acidified, and extracted with ether. From the ether layer, 4S4SH was eventually isolated, making this the first truly successful synthesis of the ligand. It was soon established that 3S4SH and 3S3SH (4,8-dithio-1,11-undecanedithiol could be made this way as well (figure 3.6). Yields tended to be low (generally in the teens), and the cost of the cesium reagent was significant, but the compounds could be synthesized by this method.

3.2 The Use of the New Thiol Ligands in Mercury Precipitation

At this point the author had four thiol ligands, three new ligands made by the method described above and the already known (but not previously used for mercury precipitation) 3S2SH, whose synthesis was described in section 2.2 (figure 3.6). All of these dithiols were evaluated for their effectiveness in precipitating mercury from water. This was accomplished by adding them as solutions in THF to 30 ppm mercury solutions (mercuric chloride in water) in 1:1, 2:1, and 3:1 molar ratios. In all cases this resulted in the formation of a white precipitate. The solutions were then filtered using 0.2 µm syringe filters and the filtrate analysed for mercury using cold vapor atomic fluorescence spectroscopy (table 3.1).

The results were found to vary significantly by ligand used, with 4S4SH giving the worst overall result and 3S4SH giving the best. It is likely that the 4S4SH ligand’s relatively poor performance was due to solubility issues, since this proved to be the least soluble of the set.



3S2SH

3S3SH

3S4SH

4S4SH

Figure 3.6: Ligands analyzed for mercury removal

Ligand	Ratio of Ligand to Mercury	Initial Mercury Concentration (ppb)	Mercury Concentration after Addition of Ligand (ppb)	Percent of Mercury Removed
3S2SH	1:1	30000	538	98.2
3S2SH	2:1	30000	666	97.8
3S2SH	3:1	30000	635	97.9
3S3SH	1:1	30000	2714	91.0
3S3SH	2:1	30000	367	98.8
3S3SH	3:1	30000	119	99.6
3S4SH	1:1	30000	214	99.3
3S4SH	2:1	30000	7	100
3S4SH	3:1	30000	0	100
4S4SH	1:1	30000	1269	95.8
4S4SH	2:1	30000	2101	93.0
4S4SH	3:1	30000	2152	92.8

Table 3.1: The removal of mercury from water by the author’s chelates

With all ligands and ratios, however, at least 90% of the mercury was removed. In the case of the 3S4SH ligand, at all ratios, over 99% of the mercury was removed and with the 3:1 ratio, the mercury concentration in the filtrate was below the detection limits of the instrument used.[252] All of these ligands proved to be highly effective mercury removal agents, comparable to the commercially available DMDTC ligand (with hopefully a greater stability in the precipitates) and superior to the TC and TMT reagents.[181] In fact, the 3S4SH gave results that were as good and perhaps slightly better than those obtained with this group's own $BDETH_2$ ligand, which is arguably the best known compound for removing mercury from water.

To further investigate the nature and stability of the mercury precipitates, the 1:1 and 3:1 ratio reactions were repeated at much higher concentrations so as to generate enough precipitate to study. As before, a white precipitate appeared immediately upon addition of the ligand in THF to the mercury solutions. The precipitate was isolated by filtration and analyzed by IR, mass spectroscopy, thermogravimetric analysis (TGA), and elemental analyses (%C, H, and S).

The results, especially the mass spectra, suggested the presence of the expected ligand-mercury complex. However, it seemed clear that there was more to the precipitates than just that simple compound. Many of the IR spectra showed a slight thiol peak, suggesting that not all of the terminal sulfurs were fully bound to mercury. The TGA's showed a steady loss of essentially all of the compound's mass for all the precipates. The mass loss occurred over different temperature ranges for each ligand used; however, for a given ligand the decomposition occurred in approximately the same temperature range for both the 1:1 and 3:1 precipitates. For some of the compounds, there was a slight change in slope for the decomposition curve during the course of the run. These could indicate different weight loss events, possibly the loss of excess ligand followed by the decomposition of the main ligand-mercury complex. However, it should be noted that the curves are just changing slope, rather than actually flattening, and that this is not seen for all the compounds. Therefore, it is difficult to definitely characterize these as truly separate events in the precipitates' decomposition.

The elemental analyses proved to be the decisive factor in characterizing these compounds. In the case of every precipitate, except that resulting for 3S3SH ligand in a 1:1 ratio with mercury, the %C, H, and S was higher than predicted for one ligand binding to one mercury. Furthermore, the reaction involving excess ligand always produced precipitates with a higher %C, H, and S than the reactions with a stoichiometric amount of ligand. The analysis was consistent with the precipitation of excess ligand with the mercury-ligand complex, except in the case of the previously mentioned 3S3SH compound, where the analyses agrees with a ratio of approximately two ligand to three mercury. The presence of this extra, still fully thiolated ligand in the majority of the precipitates also accounts for the SH peaks observed in the IR spectra.

This adsorption of extra ligand to the precipitates helps to explain why a greater mercury removal was observed when excess ligand was added. If the ligand and mercury are combined in a 1:1 ratio, then every molecule of ligand that absorbs to precipitate is not available to bind a mercury atom. This is why excess ligand should be used to maximize the precipitation of mercury. There would presumably be fewer absorption issues in a more dilute solution, but excess ligand is still logical. The more ligand that is present in a dilute solution, the more likely it is to find and precipitate all of the mercury, especially if the filtration is performed very quickly after the addition of the ligand, as it was here. Therefore, in order to quantitatively precipitate mercury with these ligands both a high excess of ligand and very dilute solutions of both mercury and ligand should be used.

3.3 Leaching Studies

To examine the long-term stability of the precipitates, leaching studies were performed. Acidic as well as neutral water was used for the leaching studies because mercury-contaminated waters, such as mine runoffs, tend to be acidic. Furthermore, mercury (like many metals) tends to form an insoluble oxide in the presence of hydroxide, therefore leaching into high pH waters was not viewed as an area of great concern. A small amount of precipitate (0.20 g - 0.26 g) was added to 100 mL of water buffered at either pH 2 or pH 7; the mixture was stirred for a short period and then left undisturbed for 53 days. At the end of this period, three 10 mL aliquots were removed, syringe-filtered, and analyzed for mercury concentration by CVAAS. Overall, the results (table 3.2) are very positive; in only one sample was the average concentration greater than 10 ppb and the majority of the samples contained less that 1 ppb mercury. A number of samples (once corrected for the slight background mercury in the blanks) contained no mercury at all. For several of the compounds, there was greater leaching in the neutral solution than in the acidic one. While initially counterintuitive, this suggests that the major mechanism for leaching in these compounds is not acidic attack on the mercury-sulfur bond. Therefore, these ligands could be very good choices for *in situ* remediation of acidic waste streams

In summary, the desired ligands have been synthesized, albeit without the yield or cost-effectiveness initially desired, and have proven to perform as intended. Not only does 3S4SH remove mercury almost quantitatively, but the resulting precipitates appear to be stable, as hypothesized. The relatively lesser removal of mercury by the 4S4SH ligand appears to be a result of its lower solubility in a water/THF mix, rather than due to any inherent difference in its chemistry, as indicated by the analysis of the precipitates and the leaching studies. Furthermore, it must be kept in mind that these results were generated by simply adding unmodified ligand in an organic solvent to the mercury solution. Unlike the commercial reagents mentioned above,

Ligand and ratio	PH	Hg Concentration after leaching study (ppb)
3S2SH 1:1	2	0.0
	7	3.5
3S2SH 3:1	2	0.1
	7	5.6
3S3SH 1:1	2	0.1
	7	14.7
3S3SH 3:1	2	0.0
	7	0.1
3S4SH 1:1	2	0.0
	7	0.4
3S4SH 3:1	2	0.0
	7	0.0
4S4SH 1:1	2	0.0
	7	0.0
4S4SH 3:1	2	0.0
	7	0.0

Table 3.2: Results of the leaching study

these ligands were not used as water soluble group 1 metal thiolates. It would be expected that the thiolate version might be even more effective. It appears that an improved synthesis of these ligands (perhaps achievable by simply refining the current method to recycle unreacted material and the cesium salts) and the development of water-soluble thiolate variations are worthy areas of further study.

Experimental Section

All reagents were purchased from Aldrich or Acros chemical companies and were reagent grade or better unless otherwise noted. NMR measurements were taken on a Varian Gemini 200 MHz NMR Spectrometer. IR spectroscopy was performed using either a Perkin Elmer model 1600 FT-IR spectrophotometer or a Nicolet Magna 560 FT-IR. Mass spectral data was gathered using a JEOL JMS-700T magnetic sector instrument or a Shimadzu QP2010S instrument. Elemental analysis was performed by Galbraith Laboratories in Knoxville, TN. The percentage of carbon and hydrogen was determined by combustion according to the ASTM D5373 and D5291 methods. The percentage of sulfur was determined by combustion according to ASTM D4239 Method B and ASTM D1552. There was a ± 0.5% uncertainity in the measurements. Thermogravimetric analysis was performed by Edison Laboratories in Schenectady, NY, using a TA Instruments YGA2950, with a N_2 flow of 100 mL/min and a heating rate of 10° C/min.

3S3SH: Cesium carbonate (40.2 g, 124 mmol) was suspended in approximately 250 mL of DMF and allowed to stir for 20 min, followed by addition of 1,3-propanedithiol (15.0 mL, 148 mmol). This white suspension was stirred for 30 min. 1,3-Diiodopropane (5.70 mL, 49.4 mmol) was then added dropwise via a dropping funnel and the mixture left to stir for 48h. The DMF was removed by heating the suspension under vacuum in a mineral oil bath. The remaining white solid was acidified with dilute HCL (this proved to be a significantly exothermic reaction) and extracted with methylene chloride. The methylene chloride layer was distilled between 143-146°C at 0.4 mm Hg, yielding the product. Yield: 4.30 g (16.8 mmol), 34%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 1.32 (t, 2H), 1.69-1.98 (m, 6H), 2.47-2.75 (m, 12H), ^{13}C NMR ($CDCl_3$, 200 MHz,):

d 33.0, 30.5, 30.0, 29.0, 23.2, IR (thin film on NaCl plates, cm^{-1}) 2922(s), 2844(m), 2564(m), 1650(w), 1605(w), 1440(s), 1342(w), 1296(m), 1250(s), 1206(w), 1028(w), 958(w), 838(w), 758(w), 654(w), GC-MS: peak at RT= 16.236 min, *m/z* = 256 (M$^+$), purity by GC: 90.6%.

3S4SH: Cesium carbonate (75.0 g, 230 mmol) was suspended in DMF along with butanedithiol (45.0 mL, 384 mmol). This was stirred for 3 h, and then dibromopropane (8.81 mL, 76.7 mmol) was slowly added in 100 mL DMF. The mixture was stirred for approximately 48 h, and then the DMF was removed via heating under vacuum. The residue was acidified, then extracted with methylene chloride. When the organic layer was removed via vacuum, the residue was found to be a mixture of butanedithiol and 3S4SH. This was distilled between 149-156°C at 0.4 mm Hg. Yield: 2.10 g (7.39 mmol), 10%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 2.39 (m, 12H), 1.75 (t, 2H), 1.55 (m, 10H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 32.9, 31.4, 30.8, 29.2, 28.1, 24.1, IR (thin film on NaCl plates, cm^{-1}) 2930(s), 2848(s), 2546(w), 1708(w), 1638(w), 1436(s), 1342(w), 12.82(m), 1246(m), 1202(w), 1132(w), 1026(w), 994(w), 914(m), 840(w), 724(m), 652(w), GC-MS: peak at RT=21.10 min, *m/z* = 284 (M$^+$), purity by GC: 97.2%.

4S4SH: Cesium carbonate (21.1 g, 64.9 mmol) was suspended in approximately 350 mL of DMF. To this suspension was added technical grade (90%) 1,4-butanedithiol (10.0 mL, 76.7 mmol). The suspension was stirred for 30 min, followed by slow addition of 1,4-diiodobutane (4.00 mL, 30.2 mmol) and 48 hours of stirring at room temperature. The DMF was then removed by heating under vacuum, and the residue was acidified with dilute HCl. The acidic solution was extracted with methylene chloride. The methylene chloride layer was distilled between 181-189°C at 0.4 mm Hg. Yield: 1.00 g (3.34 mmol), 11%, ^{1}H NMR ($CDCl_3$, 200 MHz): d 2.52 (m, 12 H), 1.73 (m, 12H), 1.38 (t, 2H), ^{13}C NMR ($CDCl_3$, 200 MHz): d 32.8, 31.5, 31.3, 28.5, 28.0, 24.1, IR (thin film on NaCl plates, cm^{-1}): 2930(s), 2852(s), 2546(w), 1708(w), 1638(w), 1450(s), 1350(w), 1280(s), 1238(m), 1202(w), 1178(w), 1134(w), 1026(w), 1002(w), 914(m), 724(m), 652(w), GC-MS: peak at RT= 20.12 min, m/z = 298 (M^+), purity by GC: 97.3%.

CVAFS Analysis of Ligands with Mercury: 4S4SH (0.0446 g, 0.150 mmol), 3S4SH (0.0422 g, 0.149 mmol), 3S3SH (0.0383 g, 0.150 mmol), and 3S2SH (0.0385 g, 0.167 mmol) were each added to separate 100 mL volumetric flasks, which were then filled to the line with THF. A 1 mL, a 2 mL, and a 3 mL aliquot from each ligand solution was added to separate 10 mL aliquots of a 30 ppm mercury in water stock solution (giving a total of 12 samples). Upon addition of ligand solution, all the mercury samples immediately became white and cloudy. Each sample was filtered with a 0.2 µm syringe filter prior to analysis. The CVAFS analysis was performed by the author, using a Vasal VI2000 atomic fluorescence spectrometer, calibrated using standard solutions to accurately measure mercury concentrations of between 0 and 30 ppb and with an accuracy of ±1 ppb. Samples were initially run at a 200:1 dilution factor, then gradually analyzed at higher concentrations until they yielded values located upon the calibration curve. All readings were taken in triplicate or better to ensure reproducibility.

3S2SH + $HgCl_2$ in a 1:1 Ratio: Mercury chloride (1.19 g, 4.38 mmol) was dissolved in 35 mL of DI water. To this was added 3S2SH (1.00 g, 4.39 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate the solid, identified as 3S2SHg ·0.5 3S2SH. Yield: 0.369 g (0.683 mmol), 23%**,** IR (KBr Pellet, cm^{-1}): 2935(s), 2823(m), 2523(w), 1634(w), 1427(m), 1407(m), 1331(w), 1303(s), 1265(m), 1204(m), 1144(m), 1018(w), 988(w), 900(m), 848(m), 801(w), 723(w), 692(w), 666(w), 634(w), Mass Spectrum: *m/z* = 427 ($3S2SHg^+$), TGA: one mass loss from 190°C-345°C of 83.83%, one mass loss from 345°C-410°C of 13.19%, Anal. for 3S2SHg ·0.5 3S2SH, Calcd. (Found): C 23.28% (22.99%), H 4.09%(3.92%), S 35.52% (35.85%).

3S2SH + $HgCl_2$ in a 3:1 Ratio: Mercury chloride (1.18 g, 4.21 mmol) was dissolved in 40 mL of DI water. To this was added 3S2SH (2.88 g, 12.6 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate the solid, identified as 3S2SHg ·1.4 3S2SH. Yield: 1.22 g (1.63 mmol), 39%, IR (KBr Pellet, cm^{-1}): 2903(s), 2810(m), 2515(w), 1621(w), 1423(m), 1407(s), 1329(w), 1302(m), 1265(m), 1206(m), 1143(m), 1005(w), 959(w), 899(m), 847(m), 793(w), 723(w), 693(m), 663(w), 634(w), Mass Spectrum: *m/z* = 427 ($3S2SHg^+$), TGA: one mass loss from 165°C-440°C of 96.90%, Anal. for 3S2SHg ·1.4 3S2SH, Calcd. (Found): C 27.02% (33.56%), H 4.91% (4.63%), S 41.21% (41.49%).

3S3SH + $HgCl_2$ in a 1:1 Ratio: Mercury chloride (1.59 g, 5.86 mmol) was dissolved in 40 mL of DI water. To this was added 3S3SH (1.50 g, 5.86 mmol) in 10 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate the solid, identified as $(3S3S)_{0.67}HgCl_{0.66}$. Yield: 1.33 g (3.38 mmol), 58%, IR (KBr Pellet, cm^{-1}): 2914(s), 2841(m), 2489(w), 1667(w), 1590(w), 1442(s), 1334(m), 1293(w), 1242(m), 1182(w), 1044(w), 1000(w), 953(w), 846(w), 740(m), 660(w), Mass Spectrum: *m/z* = 455 ($3S3SHg^+$), TGA: one mass loss from 150°C -245°C of 16.45%, one mass loss from 245°C-500°C of 78.63%, Anal. for $(3S3S)_{0.67}HgCl_{0.66}$, Calcd. (Found): C 18.39% (17.97%), H 2.92% (2.97%), S 21.82% (22.96%).

3S3SH + $HgCl_2$ in a 3:1 Ratio: Mercury chloride (1.59 g, 5.86 mmol) was dissolved in 40 mL of DI water. To this was added 3S3SH (4.5 g, 17.6 mmol) in 20 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 3S3SHg ·1.3 3S3SH. Yield: 1.61 g (2.05 mmol), 35%, IR (KBr Pellet, cm^{-1}): 2915(s), 2844(m), 2544(w), 1636(w), 1430(s), 1384(w), 1337(w), 1294(w), 1247(s), 1198(w), 1046(w), 955(w), 844(w), 741(w), 668(w), Mass Spectrum: Highest mass at *m/z* = 382 ($3S3SHgH^+$ minus $(CH_2)_3S$), TGA: one mass loss from 110°C -370°C of 85.69%, one mass loss from 370°C-530°C of 10.93%, Anal. for 3S3SHg ·1.3 3S3SH, Calcd. (Found): C 31.48% (31.34%), H 5.61% (5.33%), S 37.35% (37.59%).

3S4SH + $HgCl_2$ in a 1:1 Ratio: Mercury chloride (1.43 g, 5.27 mmol) was dissolved in 40 mL of DI water. To this was added 3S4SH (1.50 g, 5.28 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 3S4SHg ·0.8 3S4SH. Yield: 1.81 g (2.56 mmol), 87%, IR (KBr Pellet, cm^{-1}): 2919(s), 2854(m), 1634(w), 1430(s), 1339(w), 1307(m), 1248(m), 1190(m), 1113(w), 993(w), 913(w), 872(w), 738(m), Mass Spectrum: Highest mass at *m/z* = 396 ($3S4SHgH^+$ minus $(CH_2)_4S$); TGA: one mass loss from 105°C -380°C of 99.43%, Anal. for 3S4SHg ·0.8 3S4SH, Calcd. (Found): C 33.41% (33.51%), H 5.83% (5.72%), S 32.43% (32.19%).

3S4SH + $HgCl_2$ in a 3:1 Ratio: Mercury chloride (1.43 g, 5.27 mmol) was dissolved in 40 mL of DI water. To this was added 3S4SH (4.50 g, 15.8 mmol) in 15 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 3S4SHg ·2.7 3S4SH. Yield: 1.56 g (1.25 mmol), 29.3%, IR (KBr Pellet, cm^{-1}): 2919(s), 2854(m), 2510(w), 1625(w), 1431(s), 1340(w), 1308(m), 1251(m), 1190(m), 1048(w), 910(w), 872(w), 739(m), 668(w), Mass Spectrum: Highest mass at *m/z* = 396 (3S4SHgH$^+$ minus $(CH_2)_4S$), TGA: one mass loss from 100°C -380°C of 98.51%, Anal. for 3S4SHg ·2.7 3S4SH, Calcd. (Found): C 39.06% (38.54%), H 6.99% (6.81%), S 37.92% (39.95%).

4S4SH + $HgCl_2$ in a 1:1 Ratio: Mercury chloride (0.319 g, 1.17 mmol) was dissolved in 30 mL of DI water. To this was added 4S4SH (0.350 g, 1.17 mmol) in 10 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 4S4SHg ·0.1 4S4SH. Yield: 0.442 g (0.834 mmol), 78%, IR (KBr Pellet, cm^{-1}): 2927(s), 2855(m), 1558(w), 1445(s), 1304(m), 1277(m), 1227(w), 1199(m), 1110(w), 983(w), 933(w), 900(w), 731(m), 668(w), Mass Spectrum: Highest mass at *m/z* = 411 (4S4SHgH$^+$ minus $(CH_2)_4S$), TGA: one mass loss from 130°C -220°C of 54.77%, one mass loss from 220°C-415°C of 44.40%, Anal. for 4S4SHg ·0.1 4S4SH, Calcd. (Found): C 30.18% (30.65%), H 5.11% (4.54%), S 26.86% (26.13%).

4S4SH + $HgCl_2$ in a 3:1 Ratio: Mercury chloride (0.319 g, 1.17 mmol) was dissolved in 30 mL of DI water. To this was added 4S4SH (1.05 g, 3.52 mmol) in 11 mL of HPLC grade THF. Upon addition of the ligand, a white precipitate immediately formed. The suspension was filtered to isolate this solid, identified as 4S4SHg ·1.9 3S4SH**.** Yield: 0.538 g (0.502 mmol), 43%, IR (KBr Pellet, cm^{-1}): 2922(s), 2856(m), 2490(w), 1667(w), 1441(s), 1305(m), 1278(m), 1233(w), 1199(w), 1070(w), 1048(w), 730(w), 668(w), Mass Spectrum: Highest mass at *m/z* = 411 (4S4SHgH$^+$ minus $(CH_2)_4S$), TGA: one mass loss from 175°C -380°C of 99.98%, Anal. for 4S4SHg ·1.9 3S4SH, Calcd. (Found): C 39.32% (39.77%), H 6.96% (6.89%), S 34.99% (34.32%).

Leaching Studies: One Metrepak pHydrion buffer capsule (either pH 7.00 ± 0.02 or pH 2.00 ± 0.02) was dissolved in 100 mL of DI water. Between 0.20g-0.26g of one of the mercury ligand precipitates was weighed into each solution, then stirred vigorously, covered with parafilm, and left in a fume hood for 53 days. Three 10 mL aliquots from each sample were then filtered through a Corning 0.20 µM syringe filter. The resulting forty-eight samples (along with three DI water blanks) were analyzed for mercury concentration at the University of Kentucky Environmental Research and Training Laboratory with a QuickTrace M-7500 cold vapor atomic absorption spectrometer, with an accuracy of ±0.1 ppb.

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Chapter Four: A Quantification of Geometry for Four-Coordinate Compounds

4.1 The Four-Coordinate Geometric Parameter

As mentioned above, one major focus of the Atwood research group has long been the study of group thirteen metals such as aluminum and gallium. The primary contribution of the author to these endeavors has been the writing of a pair of reviews on the subject.[253, 254] During the course of writing one of those papers, the author became interested in the quantification of the geometry of four-coordinate compounds. This was not only an interesting idea for group thirteen compounds, but it also tied into the author's main research, which involved trying to make four-coordinate complexes around mercury. Therefore, the author chose to structure one of the papers[254] around a new formula he had devised to assign numerical values to the geometry of four-coordinate metal ligand complexes. This chapter will concern the development of that equation and its application to both group thirteen and mercury compounds.

At this point, it would be worthwhile to consider what is meant by the quantification of geometry. To illustrate, consider the case of four-coordinate group thirteen compounds. These are generally classified as being one of two main geometries, either tetrahedral (Td) or trigonal monopyramidal (TMP). However, the true geometry of a given compound tends to lie somewhere between the ideals. Furthermore, this matter of geometry can be quite important for four-coordinate aluminum and gallium, because many of these species have catalytic properties for various Lewis acid-mediated polymerizations[255, 256] and the active catalyst usually coordinates a fifth substituent. A TMP geometry possesses an open coordination site and, in the absence of any steric effects, would provide the ideal coordination environment for a fifth ligand.

A square planar geometry (a highly unlikely geometry for a group thirteen compound) would provide two such sites. Therefore, for catalytic applications and assuming all ligand effects are equal, a compound that possesses a geometry close to trigonal monopyramidal would be expected to be a superior Lewis acid by comparison to one adopting the more common tetrahedral geometry.[257] If a number could be assigned to a compound's geometry and if this number would accurately reflect how distorted this compound was from Td towards some geometry more likely to coordinate a fifth substituent, that value could, at a glance, convey important information about the compound. Certainly it would convey more information that the current tendency to simply refer to a compound as being "distorted" from some ideal geometry.

The idea of quantifying a compound's geometry certainly did not originate with this author. The use of "shape-determining angles" to more precisely determine the degree of a compounds distortion from its ideal geometry was first proposed by Muetterties in 1974.[258] More recently, Avnir has developed a significant body of work concerning his technique for defining a compound's true shape, known as continuous symmetry measures (CSM) or, when applied specifically to chirality, continuous chirality measures (CCM).[14, 259-264] This is a general method which involves mathematically defining the distortion (referred to by Avnir as distance) between a real compound and an ideal symmetry/geometry. In practice, this is usually presented graphically as "symmetry maps" in which two ideal geometries are picked, the "distance" between a compound and each ideal geometry is determined, and the results for a series of compounds then plotted on a scatter plot with the distances from each ideal geometry on the axes.[14, 261, 265] This is undeniably an elegant method and a good deal of information can be determined from it. In fact, this method has been applied to the optimization of copper complexes as enantioselective catalysts.[265] However, the calculations involved in determining the CSM or CCM of a compound are somewhat complicated and some study is required to elucidate useful information from the resulting data. The author was considering something simpler, which could be easily determined with a calculator and would serve as a reliable approximation of a four-coordinate compound's distortion towards a geometry more likely to coordinate a fifth substituent.

A simpler method does exist for four coordinate compounds. Developed for use in analyzing boron Lewis acid adducts, the tetrahedral character (THC) has been modified and utilized by Hopfl to compare a number of boron compounds.[266] The tetrahedral character is defined by the equation:

$$THC_{DA}(\%) = \left| 1 - \frac{\sum_{n=1-6} (109.5 - q_n)^0}{90^0} \right| \times 100 \qquad (1)$$

where ?$_{1\text{-}6}$ are the six bond angles around the metal. A compound with a THC value of 100% is perfectly tetrahedral. This method was developed to quantify the extent to which the geometry of a three-coordinate compound approaches tetrahedral upon coordination of a fourth substituent. It, in effect, measures how "tetrahedral" a compound is. Although the THC value can show that a compound is distorted from the tetrahedral geometry, it does not necessarily show what geometry the molecule has been distorted to. In light of Nelson's correlation of Lewis acidity and geometry,[257] the author was interested in distortion towards a TMP, or an unlikely square planar, geometry as a means of measuring the ability of a four-coordinate compound to coordinate a fifth ligand. It was to quantify the degree to which a compound is distorted towards one of these ideal geometries that the author decided to develop a new value, the Four-Coordinate Geometric Parameter (FCGP).

To calculate the FCGP for a compound, one must picture the structure as a three dimensional object, with each substituent as a vertex. This structure will have four triangular faces (unless the geometry is square planar, in which case the formula works but the picture doesn't) and each face will, by definition, have three angles (figure 4.1). These angles will be the substituent-metal-substituent angles from the structure. The sum of the angles around each of the four faces of the tetrahedron must be calculated and the largest face (the one where the sum of the angles is closest to 360°) determined. It should be noted that simply dividing this number by 360° would give a crude measure of the compound's distortion from a planar geometry. However, further terms have been added to refine this crude approximation. Therefore, the sum of the three remaining angles (not part of the largest face), multiplied by 5.61, is subtracted from the sum of this largest face. To this is added 1516.15. Both 5.61 and 1516.15 are simply normalization factors, which insure that the range of values run over a reasonable and readily interpretable spectrum. This combined value is then divided by 360 and multiplied by 100 to yield a reasonable range of values. A visual description of the parameter is given in figure 4.2. The entire term involving the three angles not included in the largest face is designed to correct for the situation in which the three equatorial substituents are bent above the equatorial plane (i.e., the equatorial to axial bond is less than 90°). Due to this correction, the FCGP value of a compound distorted in this manner will be greater than 100, showing that there is actually more space open for a fifth substituent than would be expected with a purely TMP complex. The value can also be greater than 100 if there are multiple faces available which are close to 360°. This possibility will be discussed in depth in the next paragraph.

To see how this formula actually works, it is necessary to look at some examples. Data such as the various angles and the sums of the angles around the various faces for every example discussed in this chapter is included in table 4.1. A perfectly trigonal monopyramidal structure will have three 90° angles (equatorial ligands to axial ligand) and three 120° angles (equitorial ligands to each other). Therefore, three faces will have a sum of 300° and one face (the

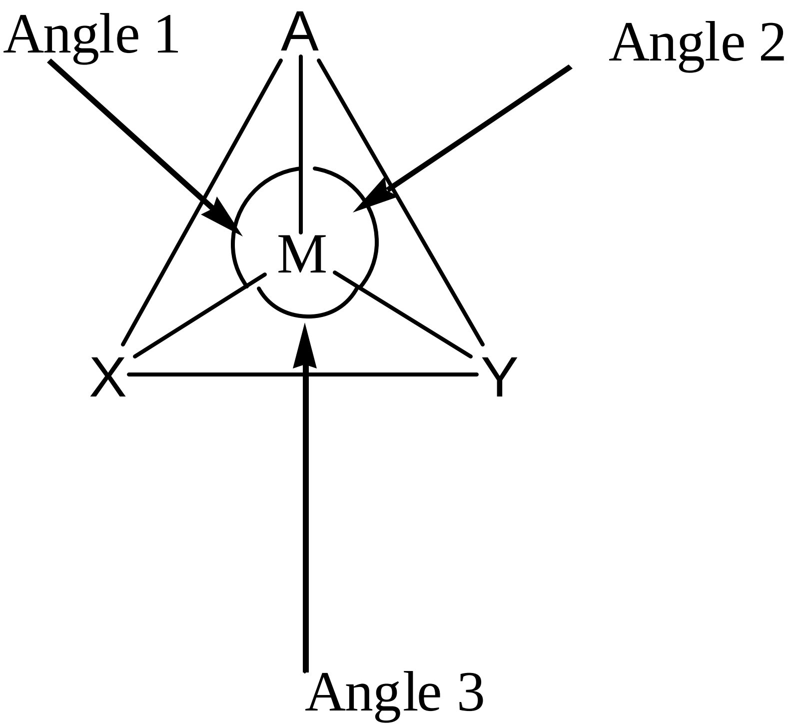
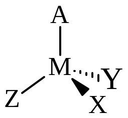


Figure 4.1: One face of a tetrahedron



Six Angles:	Four Faces:
A-M-X	(A-M-X) + (X-M-Z) + (A-M-Z)
A-M-Y	(A-M-Z) + (Y-M-Z) + (A-M-Y)
A-M-Z	(A-M-Y) + (X-M-Y) + (A-M-X)
X-M-Z	(X-M-Y) + (Y-M-Z) + (X-M-Z)
X-M-Y	
Y-M-Z	

$$\text{FCGP} \;=\; \frac{\text{largest face-(sum of remaining three angles)(5.61)} + 1515.15}{360} \;\text{X}\; 100$$

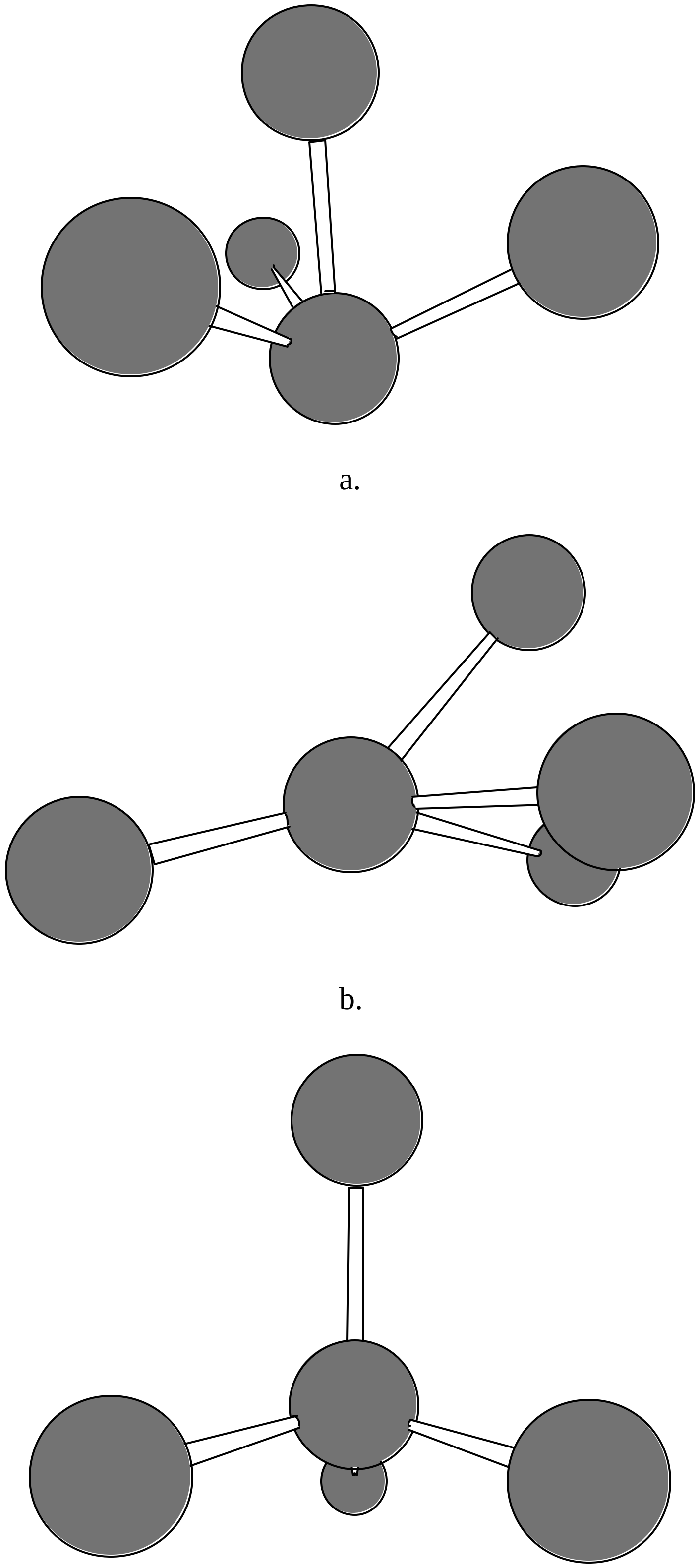
Figure 4.2: The four-coordinate geometric parameter

equatorial plane with three 120° angles) will have a sum of 360°. So to calculate the FCGP, the sum of three 90° angles (270°) multiplied by 5.61 would be subtracted from 360°. To this number would be added 1516.15 and the result divided by 360°, then multiplied by 100. This, of course, gives a FCGP value of 100. If the three equatorial substituents were forced out of this plane towards the axial substituent, so that the equatorial to axial bond angles were 70° and the equatorial to equatorial bond angles were 109° (an admittedly unlikely scenario), then the FCGP would increase to 185 **(**figure 4.3a**).** This indicates that such a structure actually has a face that is more exposed than that in classic trigonal monopyramidal geometry. As mentioned above, a value higher than 100 can also result if there a multiple faces open which are close to 360°. To use another exaggerated example, one can picture a structure in which the equatorial substituents of a trigonal monopyramidal complex are forced away from the axial substituents and towards each other, so that all three formerly equatorial substituents are now 144.7° away from the formerly axial group. This leaves these substituents each 60° from each other, so that the face which was formerly 360° is now 180°. At first glance, it would seem that the FCGP should precipitously decline due to this distortion. The beauty of the FCGP parameter, however, is that it takes into account all the faces of the tetrahedron, not just one. Although one face has become far smaller, the remaining three have grown to a much larger 349.5° **(**figure 4.3b**).** With three nearly planar faces available, clearly this structure has room to coordinate a fifth substituent. This extra room for a fifth group is accurately reflected by the FCGP value of 106. Geometrically, this structure is somewhat hard to qualify, but one could be argued that it is a significantly distorted trigonal pyramid, with two equatorial substituents drawn close to each other and the axial substituent bending towards those two equatorial bonds.

In fact, one can picture a continuum of geometries with associated FCGP values. Starting with a perfectly trigonal monopyramidal structure (FCGP=100), the three equatorial groups can

Compound	A	X	Y	Z	A-M-X	A-M-Y	A-M-Z	X-M-Z	X-M-Y	Y-M-Z	Face #1	Face #2	Face #3	Face #4	Largest face	Sum of remaining angles	FCGP
Perfect TMP					90	90	90	120	120	120	300	300	300	360	360	270	100
Perfect Td					109.5	109.5	109.5	109.5	109.5	109.5	328.5	328.5	328.5	328.5	328.5	328.5	0
Perfect square planar					180	90	90	90	90	180	360	360	360	360	360	360	-40
Perfect "See-saw"					90	90	180	90	120	90	360	360	300	300	360	300	54
Sulfur tetrafluoride[267]					87.8	87.8	173.1	87.8	101.5	87.8	348.7	348.7	277.2	277.2	348.7	277.2	86
Example 1					70	70	70	109	109	109	249	249	249	327	327	210	185
Example 2					60	60	144.74	144.74	60	144.74	349.5	349.5	180	349.5	349.5	264.7	106
Example 3					100	100	100	117	117	117	317	317	317	351	351	300	51
Example 4					105	105	105	113.5	113.5	113.5	323.5	323.5	323.5	340.5	340.5	315	25
Example 5					160	91.6	91.6	91.6	91.6	160	343.2	343.2	343.2	343.2	343.2	343.2	-18
Smith[268]	N1	Cl1a	Cl1	N1a	113.56	110.04	99.41	110.04	110	113.56	323.01	323.1	333.55	333.55	333.55	323.01	10
Lin[269]	O1	O3a	O3	O2	114.07	111.58	118.16	117.57	80.52	108.3	349.8	338.04	306.17	306.4	349.8	300.4	50
Ko and Kang[270] Ga1	N1	C13	N3	C12	107.8	79.8	109.2	129.9	113.7	105.2	346.9	294.2	301.3	348.8	348.8	296.8	56
Ko and Kang[270] Ga2	N2	S1	C10	C11	70.3	115.9	110.7	113.4	113.4	122	294.4	348.6	299.6	348.8	348.8	296.9	55
Nelson[257]	N2	C20	N1	N3	114	85.2	83.2	115.6	121.6	121.4	312.8	289.8	320.8	358.6	358.6	282.4	81
Verkade[271]	N1	N4	N2	N3	91.8	92.3	92.3	119.9	120.2	119.6	304	304.2	304.3	359.7	359.7	276.4	90
Schuman[272]	N	C1	C1'	C1"	89.2	89.2	89.2	120	120	120	298.4	298.4	298.4	360	360	267.6	104
Setzer[10]	S2	S1	S1'	S2'	91	161.6	91.4	161.6	92.4	91	344	344	345	345	345	344	-19
Sandstrom[275] HgI_2	I1	I2	S2	S1	113.2	112.2	107	111.9	108.8	103.3	332.1	322.5	334.2	324	334.2	322.2	12
Sandstrom[275] $HgBr_2$	Br1	Br2	S2	S1	112.4	109.7	106	112.7	108.4	107.5	331.1	323.2	330.5	328.6	331.1	325.6	6
Sandstrom[275] $HgCl_2$	Cl1	Cl2	S2	S1	111.8	107.7	105	114.2	108.7	109.1	331	321.8	328.2	332	332	324.5	8
Popovic[274] Structure **7**	I2	I1	S2	S1	124.43	114.86	110.8	109.41	102.9	88.36	344.64	314.02	342.23	300.71	344.64	302.06	46
Popovic[274] Structure **8**	S4	S1	S2	S3	99.8	108.1	97.1	119.3	115.6	113.2	316.2	318.4	323.51	348.11	348.11	305	43
Bell[276]	Br2	S3	S1	Br1	101.03	112.73	106.82	110.67	122.6	102.34	318.52	321.89	336.36	335.61	336.36	319.8	16
Orlandini[277]	Cl1	S3	S2	S1	94.8	108.8	106.4	110.2	129	105.5	311.4	320.7	332.6	344.7	344.7	310	34
Underhill[278]	S2	S6	S10	S5	114.44	95.26	108.31	88.52	129.5	120.97	311.27	324.54	339.17	338.96	339.17	326.32	7
Hadijikakou[279] Structure **1**	S2	Cl1	S2a	P1	101.1	108.23	140.79	103.3	99.1	97.66	345.19	346.68	308.43	300.06	346.68	303.5	44
Hadijikakou[279] Structure **2** Hg1	P1	Cl1	P1'	Cl1'	107.1	116.32	113.72	97.39	113.7	107.1	318.21	337.14	337.14	318.21	337.14	318.81	18
Hadijikakou[279] Structure **2** Hg2	S42	Cl1	Cl1'	S42'	90.11	99.2	168.11	99.2	77.21	90.11	357.42	357.42	266.52	266.52	357.42	266.52	105
Lebioda[273]	O1	O1'	Cl12	Cl11	77.5	94.6	95.4	96.7	91.7	168	269.6	358	263.8	356.4	358	265.9	106
Popovic[280] Structure **1**	Cl1	Cl2	S1	S2	92.71	107.66	107.11	104.28	111	128.31	304.1	343.08	311.34	343.56	343.56	307.48	37
Popovic[280] Structure **2**	Br1	Br2	S1	S2	105.56	93.38	103.44	101.28	105.9	138.82	310.28	335.64	304.87	346.03	346.03	302.38	46
Popovic[280] Structure **3**	S'	S	I'	I	98.67	107.64	107.64	108.56	108.6	123.06	314.87	338.34	314.87	340.18	340.18	323.95	11
Popovic[280] Structure **4**	S3	S4	S1	S2	100.8	114.01	112.34	112.97	103.4	112.45	326.11	338.8	318.2	328.81	338.8	317.16	21
Popovic[280] Structure **5**	C4	C3	S1	S2	165.6	93.35	91.5	96.43	97.46	98.02	353.53	282.87	356.41	291.91	356.41	285.95	75

Table 4.1: Geometric data for all examples

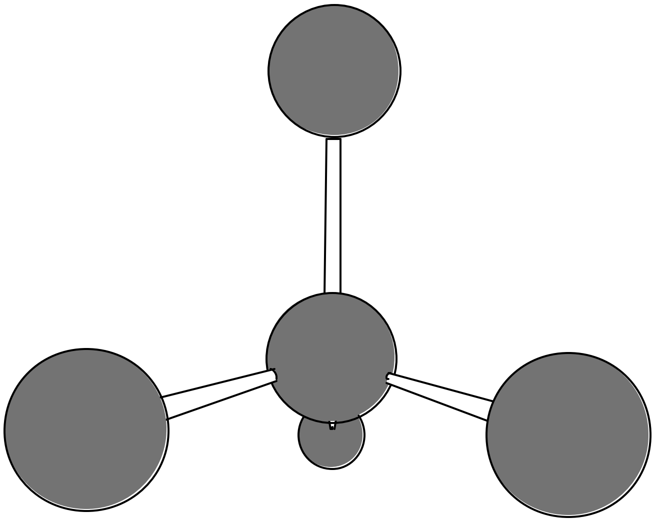


a.

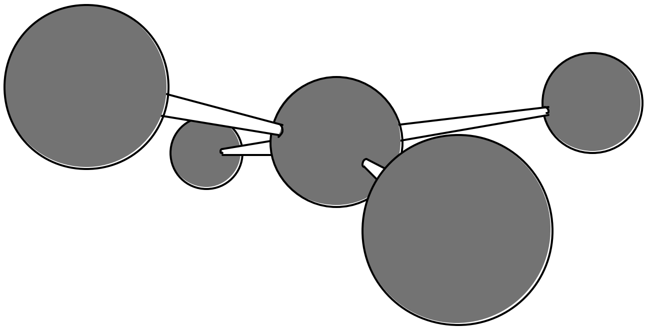
b.

c.

Figure 4.3: Examples 1-3



a.



b.

Figure 4.4: Examples 4-5

be pictured as being bent away from the axial group (and in the process begining to approach each other); as this occurs, the FCGP value drops precipitously. A change of ten degrees, placing each formerly equatorial bond 100° from the axial bond and 117° from each other, results in the FCGP dropping to 51 **(**figure 4.3c**).** A change of five more degrees (100° angles go to 105°, 117° angles go to 113.5°) results in another approximately 50% drop in FCGP, to 25 **(**figure 4.4a**).** Of course, if the same process is extended 4.5 more degrees, all angles become 109.5° and the geometry is perfectly tetrahedral, with a FCGP of 0. At this point, the structure can be further distorted in two ways; the process of forcing the originally equatorial groups away from the originally axial group can continue or all four groups can begin to be "flattened" into a plane with the central atom. If the former occurs, the FCGP will steadily rise, until the extreme case described in the paragraph above is reached.

If the latter situation occurs, one will begin to get negative FCGP values, until a square pyramidal geometry (with a FCGP of –40) is reached. For example, if this flattening is carried out to give a structure intermediate between tetrahedral and square planar, with two 160° angles and four 91.6° angles, the FCGP value is –18 (figure 4.4b). It should be noted, however, that this situation is not what the FCGP was originally created for; it was designed to measure the degree to which a structure was intermediate between a TMP geometry and a Td gemometry. While useful for information can be garnered from the FCGP for other structures, caution is necessary outside of the range of structures the formula was created for. For example, as a structure approaches a square planar geometry, the concept of "faces", as covered in the FCGP formula, has increasingly little meaning in reality. In fact, the three dimensional structure is, from a mathematical viewpoint, becoming two dimensional, i.e. a tetrahedron is becoming a square.

Another possible configuration for four-coordinate compounds is a "see-saw" geometry. This structure can be easily visualized as a trigonal bipyramid with one equatorial substituent removed. It will therefore have two axial substituents, ideally 180° apart and two equatorial substituents, ideally 120° apart from each other and 90° from the axial substituents. These angles results in two faces of 360° and two faces of 300°, yielding FCGP value of 54. This number is not as high as the 100 calculated for a TMP geometry (which would have been ideal), but is high enough to indicate the likelihood of coordinating a fifth substituent (as a "see-saw" would clearly have space to do). Furthermore, it should be noted that many compounds classified as "see-saw" have bond angles significantly different from those of the idealized structure. One reason for this is that this geometry is many times dictated by the presence of a stereochemically active lone pair on the central atom, which results in repulsion of the other substituents and a lessening of the bond angles. For example, SF_4 is often presented as the textbook example of this geometry; its axial to axial bond angle is 173° rather than 180°, with an axial to equatorial bond angle of ~88° and an equatorial to equatorial bond angle of only 101.5°.[267] This results is an FCGP of 86, which is quite reasonable for a structure with that much room to coordinate a fifth substituent. A "see-saw" is also seen for several mercury compounds, a situation that will be discussed later in this chapter when the FCGP is applied to mercury.

While a systematic attempt to apply the FCGP to compounds of a square planar or "see-saw" geometry has not been made, this intial study of those geometries appears to indicate one other useful result; compounds with a higher positive FCGP will gain a trigonal bipyramidal structure upon coordination of a fifth substituent, while those with a negative FCGP are more likely to become square pyramidal. For every example analyzed in this study, an FCGP between 50-0 has indicated a compound with a (sometimes quite distorted) tetrahedral geometry, a negative FCGP has indicated a square pyramidal geometry, and an FCGP in the 50-100 (or slightly above) range has indicated either a trigonal monopyramidal geometry or a “see-saw” geometry.

4.2 Application of the Parameter to Group 13 Structures

To test the usefulness of this parameter, it was applied to a number of aluminum and gallium compounds already reported in the literature. Although it would be neither appropriate nor beneficial to give a full review of four-coordinate aluminum and gallium chemistry as part of this dissertation, it is worthwhile to note that the formula has been shown to work for a wide range of aluminum and gallium compounds.

One literature example of an almost perfectly tetrahedral structure is presented by the work of Milton Smith III.[268] He prepared a series of compounds utilizing the bidentate chelate Li[(*p*-tol)NC(CH_3)CHC(CH_3)N(*p*-tol)]. Among other reactions, this ligand was combined with $AlCl_3$, resulting in the formation of $AlCl_2$ [(*p*-tol)NC(CH_3)CHC(CH_3)N(*p*-tol)] (figure 4.5). The compound has a planar Al-N-C-C-C-N ring, while the ligand has a bite angle of 99.4°. Beyond the distortion created by this bite angle, the compound has a clearly very tetrahedral geometry around Al, which is confirmed by the small FCGP value of 10. Although none of the angles are exactly 109°, as expected for a tetrahedral compound, they do average out to give faces of 323.0° and 333.6°, quite close to the 328.5° faces expected for a tetrahedral compound. So the FCGP value quite accurately reflects the geometry of the compound.

Another compound analyzed with the FCGP formula was a potential catalyst suggested by Lin.[269] The ligand used here is very similar to the well known Salen class of ligands used in the author’s group, except the Salen’s diimine or amine backbone is replaced by a simple methylene group linking two di-*tert*-butylphenols. When this ligand is combined with trimethylaluminum, a dimer (the structure of which was not reported in detail) forms, with both

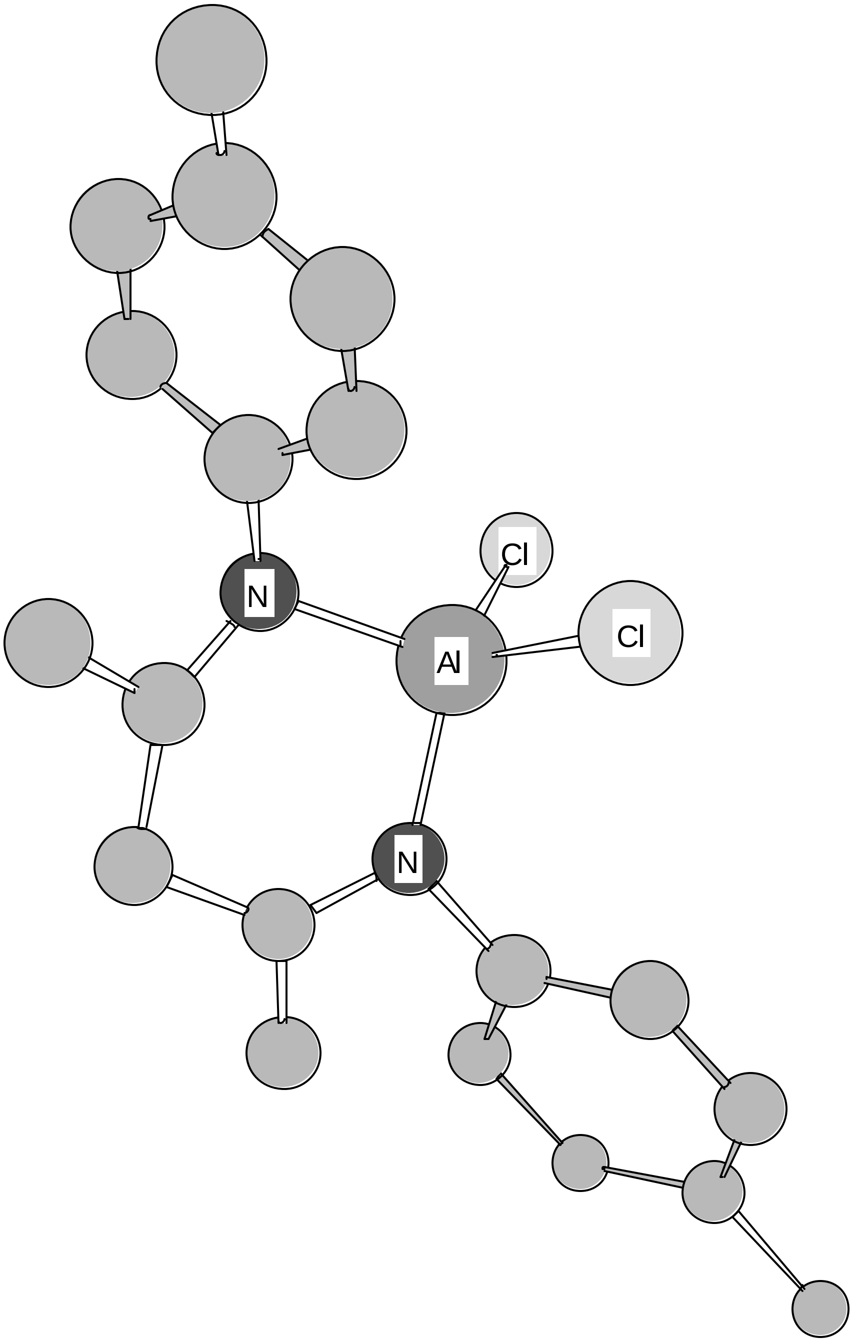


Figure 4.5: Smith's structure[268]

the phenol oxygens bound to aluminum and two molecules of methane liberated. If this compound is combined with benzyl alcohol at room temperature, the remaining methane is released and a new dimer results, with the two phenols each bound to a separate aluminum and the benzyl alcohols bridging (figure 4.6). This compound has an unusually large chelate bite angle (the most obtuse angle around the metal) of 118.2°. It also has an FCGP of 50, exactly intermediate between a tetrahedral and a trigonal monopyramidal geometry. This intermediate status is also shown by the faces; the compound's largest face was ~350°, lying between the 360° face of a trigonal monopyramidal compound and the 328.5° faces of a tetrahedral one. Not surprisingly, based on the potential relationship between geometry and catalytic activity discussed earlier, this compound was an active catalyst for the ring-opening polymerization of lactones and caprolactones and studies by Lin and coworkers have shown that that the active species is a five-coordinate compound generated by coordination of the substrate.

Another compound demonstrating a geometry intermediate between tetrahedral and trigonal monopyramidal was created by Ko and Kang utilizing the thiosemicarbazone $(Ph)(CH_3)C(CH_3)NN(H)C(S)N(H)HPh$).[270] This ligand, when combined with two equivalents of trimethylgallium, forms a compound with two gallium environments: N,N and N,S (figure 4.7). The first and third nitrogens are coordinated to what we will label gallium one. The compound has an acute (79.8°) bite angle and an FCGP value of 56, leaving the author tempted to refer to this compound as possessing a distorted trigonal monopryamidal geometry. The intermediate nature of the compound's geometry is reinforced by a look at the faces; the largest face (~349°) lies between that expected for a true trigonal monopyramidal structure and a true tetrahedral structure, as does the sum of the remaining angles (~297°). The second gallium is bound by the second N and the sulfur atom. The bite angle here is even more acute (70.3°), but the overall geometry is very similar to that of gallium one, with a FCGP of 55.

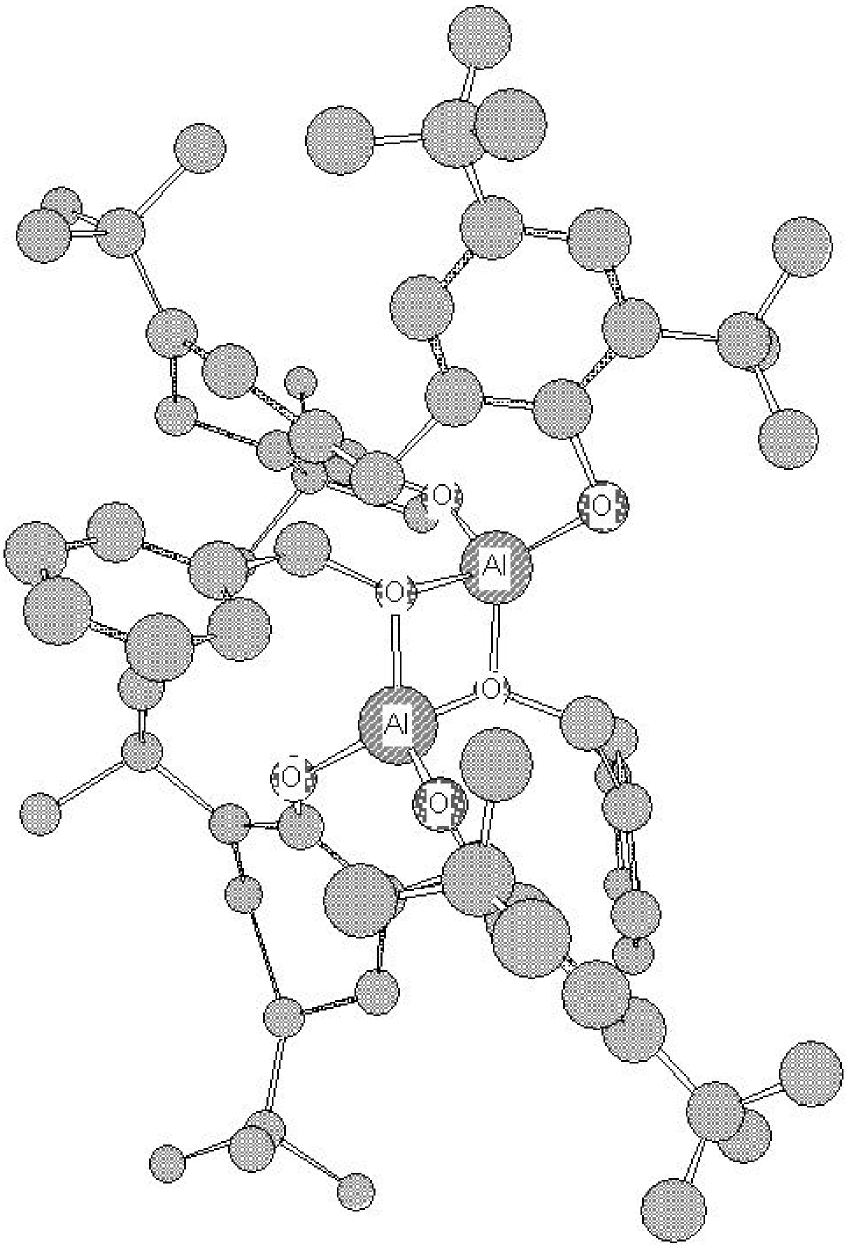


Figure 4.6: Lin's structure[269]

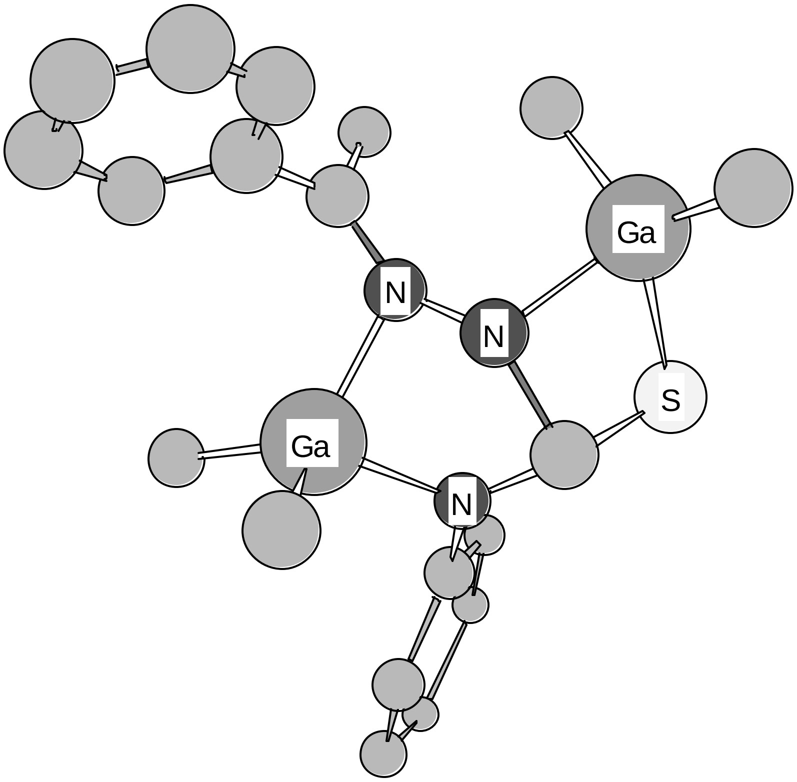


Figure 4.7: Ko and Kang's structure[270]

A compound with a significantly more pronounced trigonal monopyramidal geometry has been reported by Nelson[257] who combined the ligand, $(CF_3S(O_2)NCH(i\text{-}Pr)CH_2)_2Nbenz$ with trimethyl aluminum. The resulting structure (figure 4.8) has two nitrogens and the methyl group equatorial and the datively bonding nitrogen axial. The FCGP was 81, by far the highest encountered up to this point, but significant distortion was still introduced by the non-ligand substituent, which lay at a 114° angle from the axial nitrogen, rather than the ideal 90°. This was partly compensated for by the acute (85.2° and 83.2°) angles between the axial and equatorial nitrogens. Therefore, this compound can be pictured as having a nearly ideal trigonal plane (sum of the equatorial angles 358.6°), with the axial substituent bent slightly towards the equatorial nitrogens, rather than at a perfect 90° angle to the trigonal plane. This idea is borne out by the faces; the largest face is, rather obviously, the sum of the equatorial angles at 358.6°, very close to the ideal 360° for a trigonal monopyramidal geometry. The sum of the remaining angles (282.4°) is a little farther from the ideal of 270°, but still much closer to the expected value for trigonal monopyramidal than for tetrahedral. As predicted, it easily coordinated a fifth substituent to the open site below the trigonal plane. As expected due to their geometry, this compound, along with two other structurally analogous compounds using a variation on the ligand in which the *i*-Pr groups were removed and the benzyl replaced by a methyl group (or the entire central nitrogen replaced by an oxygen), were powerful Lewis acid catalysts for ketene-aldehyde cycloadditions. Interestingly, however, if the ligand was modified, by removing the central donor atom or lengthening the arms, to permit a more traditional tetrahedral geometry, the resulting compounds were not active catalysts. This serves to powerfully underscore the important relationship between compound geometry and catalytic activity. It also highlights the importance of relatively large arms in a chelate seeking a tetrahedral geometry, an idea that was central to the hypothesis of this thesis.

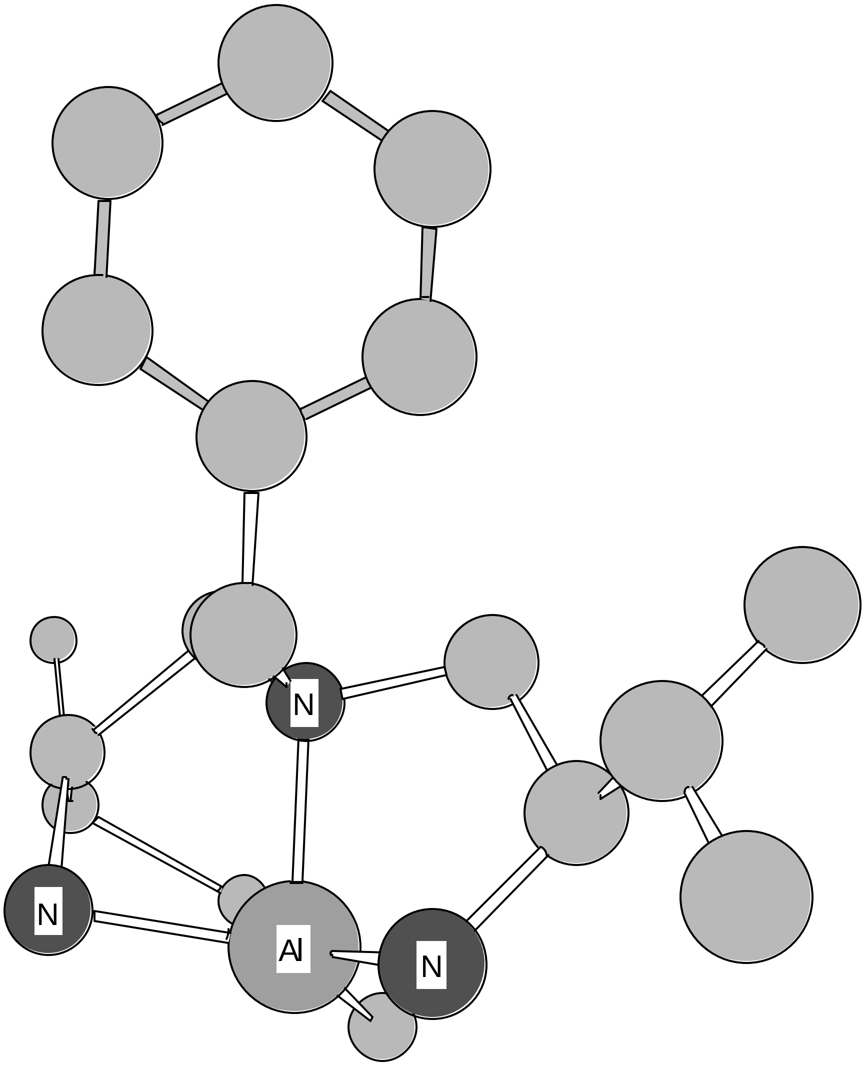


Figure 4.8: Nelson’s structure[257]

In the compound above (and other similar tridentate group thirteen chelates[255]), the primary obstacle to assuming the ideal trigonal monopyramidal geometry was the presence of one substituent that was not part of the chelate. For simple steric reasons, this substituent almost invariably was bent away from the axial substituent by a greater than ninety degree angle. Therefore, it stands to reason, if one wished to force an aluminum or gallium complex into the trigonal monopyramidal geometry, it would be wise to use a tetradentate ligand. The literature, in fact, bears out this hypothesis. One example of this is the work of Verkade[271] utilizing the trimethylsilyl azaatrane ligand $(SiMe_3HNCH_2CH_2)_3N$. This ligand is clearly similar to those used by Nelson,[257] but its third arm makes it tetradentate rather than tridentate. When it is combined with $Al(NMe_2)_3$, the resulting compound was the first example of trigonal monopyramidal geometry for aluminum (figure 4.9). The geometry is barely even distorted, with a FCGP value of 90, the sum of the equatorial angles and largest face 359.7° (for all intents and purposes planar), the sum of the three remaining angles 276.4° (just over the ideal 270°), and an average angle between an equatorial nitrogen and the axial nitrogen of 92.1°. If one equatorial nitrogen is disilylated, the loss of steric bulk permits the formation of a dimer, with the now less hindered nitrogen forming a dative bond to the open site of a second aluminum, showing that coordination of a fifth substituent is as facile for these compounds as expected.

Another atrane compound, this time reported by Schumann,[272] is even more striking. Schumann combined the tri-Grignard reagent $N[(CH_2)_3MgCl]_3$ with both aluminum and gallium chloride. He was able to resolve a crystal structure of the gallium compound, which showed it to display a trigonal monopyramidal geometry (figure 4.10). The trigonal plane was perfect, with 120° separating each carbon atom and all three carbons in a slightly acute 89.2° from the axial nitrogen. This, of course, is a real example of the situation discussed in the previous section, in which the equatorial substituents are actually bent up towards the axial, creating even more space

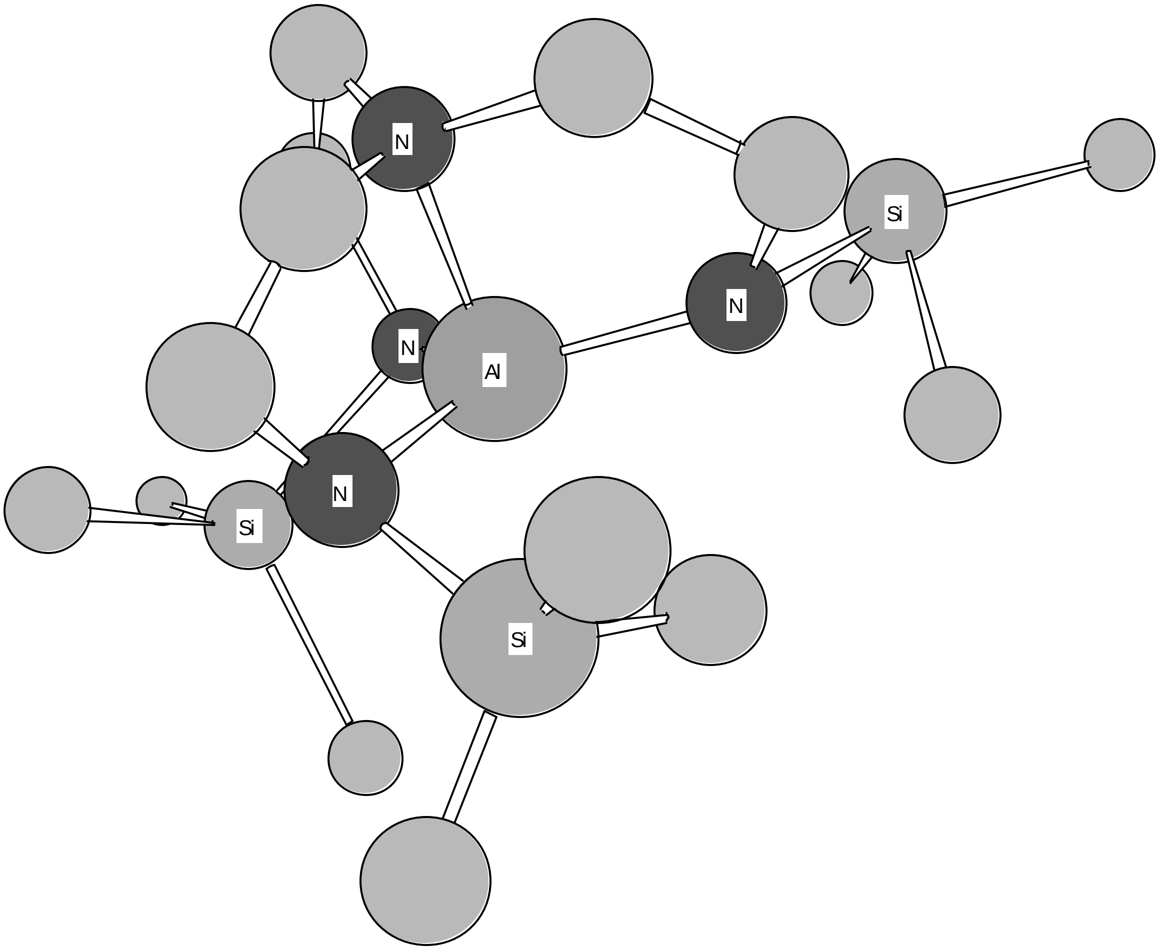


Figure 4.9: Verkade's structure[271]

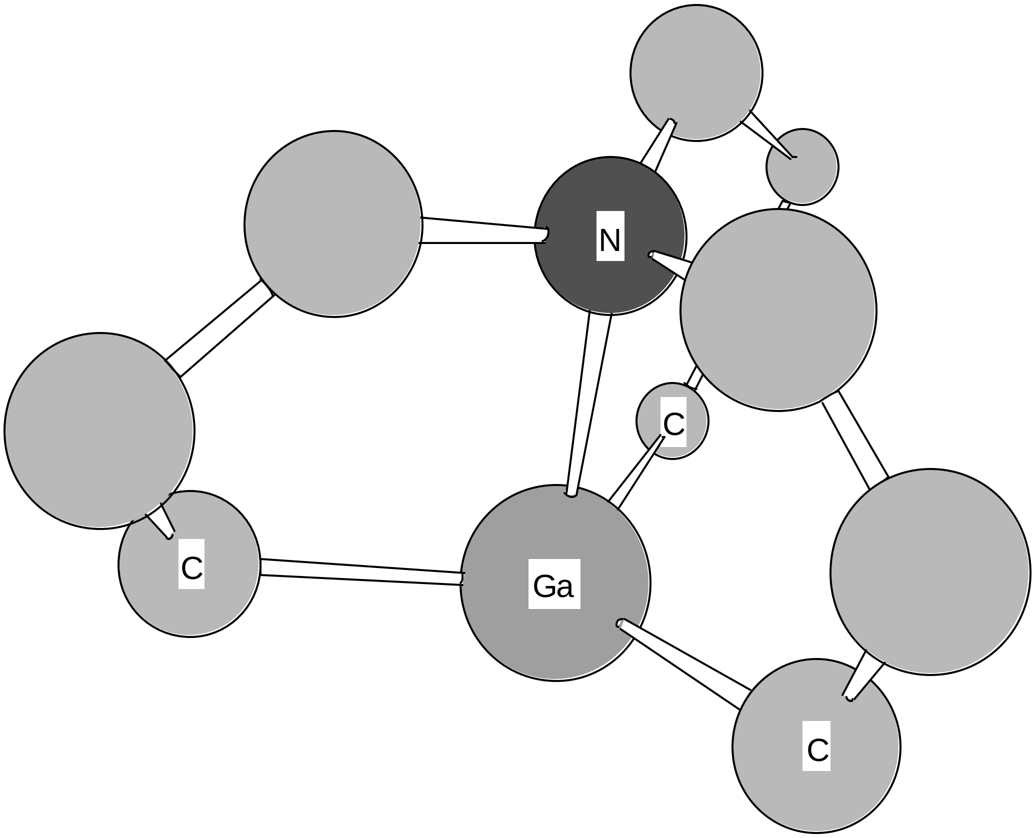


Figure 4.10: Schumann’s structure[272]

for a fifth substituent than would be predicted for a pure trigonal monopyramidal geometry. The FCGP was designed to give a value greater than 100 under these conditions and it did just that; the compound's FCGP is 104. This comes from the structure having a perfectly 360° equitorial plane (largest face) while the sum of the remaining angles is less than 270° (267.6°). This example and the ones preceeding it demonstrate that this formula is, in fact, applicable to "real life" structures.

4.3 Application of the Parameter to Mercury Structures

The Four-Coordinate Geometric Parameter was specifically designed to analyze the degree to which a group thirteen compound was distorted from a tetrahedral geometry toward trigonal monopyramidal geometry. However, as indicated earlier, the formula appears to be suitably versatile to provide useful information about other compounds and geometries. Mercury compounds have been the primary area of interest for this thesis work and therefore it seemed reasonable to apply the FCGP to a selection of them as well. Although the mercury compounds formed by the author's ligands have so far proven to be too quick-precipitating and insoluble to yield single crystals and the crystal structures necessary for FCGP analysis (as is true for most remediation agents), a number of mercury crystal structures have been reported in the literature and are therefore available for study.[10, 273-280]

As discussed in chapter one, four-coordinate mercury structures are usually classified as tetrahedral, although Holloway's review[8] did report one square planar compound.[10] Alvarez's recent discussion of the geometry of four-coordinate transition metals in general noted that a significant number of Hg^{2+} compounds could best be described as possessing a "see-saw" geometry (Alvarez referred to this as a sawhorse geometry).[14] To evaluate the usefulness of FCGP in discussing the geometry of mercury compounds, the parameter was applied to a number of structures reported in the literature, including the square planar compound from Holloway's review and several of the "see-saw" stuctures mentioned by Alvarez. The results of this study are summarized in table 4.2.

The FCGP proved quite successful in quantifying the observations of Holloway and Alvarez. The values fell into three main groupings: one compound with a negative FCGP (this was Setzer's square planar compound[10]), a few with FCGP values between 74-107,[273, 279, 280] and the majority of the compounds with FCGP values between 5-46.[274-280] The main group (FCGP 5-46) represents compounds with a tetrahedral geometry, with the higher values representing a more distorted geometry than the lower values. Since one would exepect to find a terahedral geometry for mercury, this is not a surprising result.

The group with higher FCGP values (74-107) posses a "see-saw" geometry. Alvarez had noted in his study that these "see-saw" mercury compounds generally had much longer bond lengths for the equatorial bonds than for the axial ones, leading him to conclude that they were in fact better classified as two-coordinate compounds with two other interactions. The same is true of the compounds studied here (not all of which were included in Alverez's work). This is a manifestation of mercury's tendency to take on a two-coordinate linear geometry. For example, Popovic published a study in which he treated a series of divalent mercury compounds with two equivalents of 3,4,5,6-tetrahydropyrimidine-2-thione.[280] Of the five compounds that resulted, four (made from $HgCl_2$, $HgBr_2$, HgI_2, and $Hg(SCN)_2$) have a clearly tetrahedral geometry; the fifth (made from $Hg(CN)_2$) possessed a "see-saw" geometry. Since organomercury compounds overwhelmingly favor a linear geometry,[9] this is not surprising. The result is the weakest dative interaction between mercury and sulfur (longest Hg-S bonds) of any of the compounds in Popovic's series. The other two "see-saw" geometries covered in this study do not involve organomercury compounds, but do involve especially weak dative bonds to the mercury either through bridging Cl's (both of which are covalently bonded to another Hg)[279] or through the "hard" acid oxygen[273] (a poor ligand for mercury).

Although the compounds studied here are dramatically different than those the FCGP was originally aimed at, the parameter still performed as intended. The square planar compound yielded a negative value, correctly suggesting that the addition of a fifth substituent would yield a square pyramidal geometry. FCGP values between 1-50 did in fact indicate tetrahedral compounds with varying degrees of distortion. Values above 50 indicated compounds which were geometrically well-suited to take on a fifth substituent and gain a trigonal bipyramidal geometry, although mercury accomplishes this by adopting a "see-saw" geometry rather than a trigonal monopyramidal one. These results strongly suggest that the FCGP is useful for compounds beyond the group thirteen structures it was originally designed for.

4.4 Conclusions

As has hopefully been demonstrated in the preceding pages, the FCGP equation provides a new and useful way of quantifying the geometry of some four-coordinate structures. It has proved quite successful when applied to aluminum, gallium, and mercury compounds already reported in the literature. The next step will be to expand its application to other systems. Presuming it continues to prove useful, the author hopes that it will be adopted by other chemists and widely used in the future.

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Chapter Five: Conclusions and Further Work

5.1 Conclusions and Further Work

This thesis has been focused on the design of ligands to form four-coordiante complexes with metals. The primary focus has been on the metal mercury and the main hypothesis has been that a four-coordinate sulfur-containing ligand of sufficient size to form a tetrahedral coordination environment around mercury would successfully remove mercury from water and yield stable precipitates. However, this has not been the only focus of the work. The diol compounds, a by-product of the efforts to synthesize the mercury chelates, proved to be a ligand for aluminum compounds and this led into some discussion of group thirteen chemistry. The group thirteen work culminated in the development the Four-Coordinate Geometric Parameter, which was then applied to mercury compounds as well, thereby tying the group thirteen studies back into the main focus on mercury compounds.

The impetus for this project came from the inadequacy of most current precipitating agents for mercury remediation. Agents such as DMDTC, STC, and TMT yield unstable precipitates that could potentially leach mercury back into the environment. The Atwood group aimed to design ligands which would take advantage of mercury's preferred coordination geometries (linear and tetrahedral) to give more stable precipitates. The BDET ligand was created to assume the linear geometry and, while there is no incontrovertible evidence that a BDET-Hg is in this geometry, the ligand has proven very successful at removing mercury from water and yields very stable precipitates. The dithioether dithiol ligands which are the main topic of this dissertation were designed to assume the tetrahedral geometry about mercury.

The synthesis of these ligands was not a trivial undertaking. Several unsuccessful routes were attempted before a usable path to the chelates was discovered. Many of the unsuccessful schemes, however, resulted in the synthesis of interesting side products. For example, it did not prove feasible to thiolate diol analogs of the desired ligands, but one of the diols created as a result of the efforts to do this (4S2-*tert*-OH) did form a new compound with trimethylaluminum. It would be interesting to see whether a change of conditions or solvent could create a suitable environment for growing X-ray quality crystals of this compound. Furthermore, some preliminary work not covered in this thesis suggests that the other diols created during the research react very differently with tiralkyl aluminum species. Further work should focus on how these ligands are interacting with aluminum and why they behave differently than 4S2-*tert*-OH.

As another example, efforts to thiolate diene analogs with thiolacetic acid were unseuccessful. However, the reaction of one of these dienes with $SnCl_2$ yielded the only original crystal structure reported in this work and provided an opportunity to study of the Sn^{119} NMR of shifts of a novel complex. Once again, there is ample opportunity for further work here. It would be worthwhile to see if other, similar ligands would also yield crystal structures with $SnCl_2$. Furthermore, these diene ligands could be combined with mercury, potentially yielding new organomercury compounds.

The target ligands were synthesized by the attack of two equivalents a Cs-dithiolate on a dihalide. Although yields are relatively low, this synthesis has proved repeatable and has been untilized to make multigram quantities of the compounds. These new chelates (3S3SH, 3S4SH, and 4S4SH), along with the known, but not previously used for mercury precipitation ligand, 3S2SH, proved successful at precipitating mercury from water. For a 2:1 or 3:1 excess of the 3S4SH ligand, CVAFS analysis of the treated samples detected no mercury, suggesting complete removal. The precipitates from all four ligands showed little leaching and the 3S4SH and 4S4SH precipitates leached no detectable mercury at all. These findings strongly support the central hypothesis of the thesis, namely that large, flexible dithioether dithiol ligands would remove mercury from water and form stable precipitates.

Although the current results have vindicated this approach to mercury precipitation, there is still further work that could be done with these compounds. The biggest issue with the ligands is their insolubility in water and the consequent necessity of using THF as a cosolvent when performing the mercury precipitation tests described in the previous paragraph. The obvious solution to this problem would be to create a water soluble version of the ligands, which would then be used to repeat the precipitation and leaching studies. The current leaching studies were performed over a period of approximately two months; it would also be interesting to study both the leaching and any changes in the elemental analysis of the precipitate over the course of a year or more. A study of this type would be a prerequisite before any water-soluble variant of 3S4SH or 4S4SH could be seriously considered for *in-situ* remediation. Furthermore, toxicological tests upon the ligands would be another prerequisite for *in-situ* remediation. The results of these tests could then guide future research.

As was mentioned earlier, the design of tetradentate ligands for mercury was not the only way that the author studied four-coordinate metal complexes. Another route was to develop a new method for quantifiying the geometry of such compounds. The assignment of a numerical value to a compound’s geometry makes it easier to compare compounds to each other and to spot reactivity trends that are tied to geometry. This was accomplished by the creation of a formula, based upon the six metal-to-ligand angles in a four-coordinate structure, which was dubbed the Four-Coordinate Geometric Parameter or FCGP for short. FGCP values between 0-50 represent tetrahedral (Td) geometries, with the higher values indicating an increasing distortion from an ideal Td structure. A negative FCGP value represents a square planar geometry. An FCGP value between 50-100 (or above) represents either a trigonal monopyramidal (TMP) or a “see-saw” geometry. These geometries overlap in their FCGP range because the parameter was designed to separate compounds based on the space available for a fifth substituent and the geometry that would results from such an addition. Both a TMP and a “see-saw” geometry are well suited to accept a fifth ligand and in both cases the result is a trigonal bipyramidal geometry.

The FCGP has been successfully applied to a number of compounds reported in the literature. For group thirteen structures it successfully discriminated between Td and TMP compounds. Many group thirteen complexes are catalytically active and their activity is often tied to the ability to coordinate a fifth substituent. For the group thirteen compounds studied, it was noted that catalytic activity was most often reported for those with FCGP’s of 50 or greater, which is consistent with this relationship between geometry and catalytic activity. The parameter was also successfully applied to mercury. FCGP analysis of a series of mercury structures found that the compounds fell into three basic groups, a rare square planar geometry with a negative FCGP, a common tetrahedral geometry with an FCGP between 0-50, and a “see-saw” geometry with FCGP values between 74-107. Based upon this survey, it seems that a full review of four-coordinate mercury compounds, classified by their FCGP values, might be worthwhile. It would also be interesting to apply the FCGP to Sn structures, whose stereochemically active lone pair could lead to some interesting geometries. Clearly, there is further work that can be done with the FCGP concept.

The work undertaken for this thesis has ultimately proven successful. The targeted ligands were synthesized and proved to be effective mercury precipitation agents. The resulting precipitates were stable against leaching. Several of the unsuccessful attempts to synthesize the target compounds yielded ligand byproducts upon which interesting future work can be based.

Finally, the FCGP formula has provided a new tool for the study of the geometry of four-coordinate compounds.

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