

Chapter 5

Group 12

5.1 The Group 12 Elements¹

Although the Group 12 metals (Table 5.1) are formally part of the d-block elements from their position in the Periodic Table, their electronic configuration in both their elemental form ($d^{10}s^2$) and the vast majority of their compounds (d^{10}) is that of the main group elements. The common oxidation state for all the Group 12 elements is +2, and the chemistry of zinc and cadmium compounds in particular is very similar to the analogous magnesium derivatives.

NOTE: The IUPAC (International Union of Pure and Applied Chemistry) definition of a transition metal (or transition element) states that a transition metal is "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell." Thus, Group 12 elements are not transition metals.

Element	Symbol	Name
Zinc	Zn	From German <i>zinke</i> , meaning <i>tooth-like</i> , <i>pointed</i> or <i>jagged</i> (metallic zinc crystals have a needle-like appearance), or meaning <i>tin-like</i> because of its relation to German word <i>zinn</i> meaning <i>tin</i> , or from Persian <i>seng</i> meaning <i>stone</i> .

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Cadmium	Cd	From the Latin <i>cadmia</i> , meaning <i>calamine</i>
Mercury	Hg	From the Latin <i>hydrargyrum</i> , meaning watery or <i>liquid silver</i>

Table 5.1: Derivation of the names of the Group 12 metals.

5.1.1 Discovery

5.1.1.1 Zinc

Artifacts with a high zinc content (as much as 90%) have been found to be over 2500 years old, and possibly older. As such it is clear that several cultures had the knowledge of working with zinc alloys, in particular brass (a zinc/copper alloy). Zinc mines at Zawar, near Udaipur in India, have been active since the late 1st millennium BC. However, the smelting of metallic zinc appears to have begun around the 12th century AD.

The isolation of purified metallic zinc was reported concurrently by several people. The extraction of zinc from its oxide (ZnO) was reported as early as 1668, while John Lane is supposed to have smelted zinc in 1726. The first Patent for zinc smelting was granted to English metallurgist William Champion in 1738; however, the credit for discovering pure metallic zinc is often given to Andreas Marggraf (Figure 5.1) in 1746.

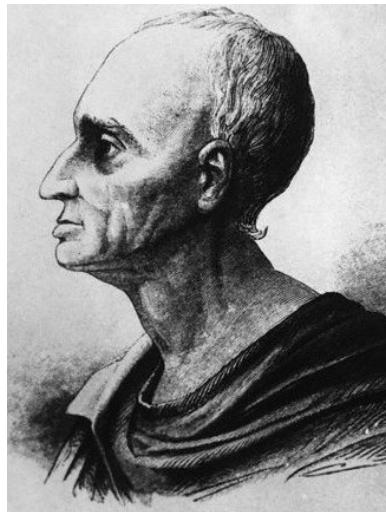


Figure 5.1: Engraving of German chemist Andreas Sigismund Marggraf (1709 – 1782).

5.1.1.2 Cadmium

Cadmium was discovered in 1817 by Friedrich Stromeyer (Figure 5.2) as an impurity in calamine (zinc carbonate, ZnCO_3). Stromeyer observed that impure samples of calamine changed color when heated but pure calamine did not. Eventually he was able to isolate cadmium metal by roasting and reduction of the sulfide.



Figure 5.2: German chemist Friedrich Stromeyer (1776 - 1835).

5.1.1.3 Mercury

Mercury was known to the ancient Chinese and was found in Egyptian tombs that date from 1500 BC. In China and Tibet, mercury use was thought to prolong life, heal fractures, and maintain generally good health. The ancient Greeks used mercury in ointments; the ancient Egyptians and the Romans used it in cosmetics that sometimes deformed the face.

5.1.2 Abundance

The Group 12 elements mainly occur in sulfide ores, however, as with their Group 2 analogs, carbonate are known, but not as economically viable. The major zinc containing ore is zinc blende (also known as sphalerite), which is zinc sulfide (ZnS). Other important ores include, wurtzite (ZnS), smithsonite (zinc carbonate, $ZnCO_3$), and hemimorphite (calamine, Zn_2SiO_4). The basic form of zinc carbonate (hydrozincite, $Zn_5(CO_3)_2(OH)_6$) is also mined where economically viable. The main source of cadmium is as an impurity in zinc blende; however, there are several other ores known, e.g., cadmoselite (cadmium selenide, $CdSe$) and otavite ($CdCO_3$). Mercury sulfide (cinnabar, HgS) is the major source of mercury, and in fact metallic liquid mercury droplets are often found in the ore. The terrestrial abundance of the Group 12 elements is given in Table 5.2.

Element	Terrestrial abundance (ppm)
Zn	75 (Earth's crust), 64 (soil), 30×10^{-6} (sea water)
Cd	0.1 (Earth's crust), 1 (soil), 1×10^{-6} (sea water)
Hg	50×10^{-6} (Earth's crust), 2×10^{-8} (soil), 40×10^{-12} (sea water)

Table 5.2: Abundance of Group 12 elements.

5.1.3 Isotopes

The naturally abundant isotopes of the Group 12 metals are listed in Table 5.3.

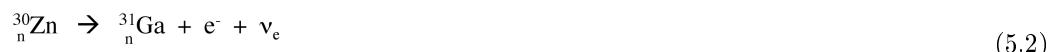
Isotope	Natural abundance (%)
Zinc-64	48.6
Zinc-66	27.9
Zinc-67	4.1
Zinc-68	18.8
Zinc-70	0.6
Cadmium-106 *	1.25
Cadmium-108 *	0.89
Cadmium-110	12.49
Cadmium-111	12.8
Cadmium-112	24.13
Cadmium-113 *	12.22
Cadmium-114 *	28.73
Cadmium-116 *	7.49
Mercury-196	0.15
Mercury-198	9.97
Mercury-199	16.87
Mercury-200	23.1
Mercury-201	13.18
Mercury-202	29.86
Mercury-204	6.87

Table 5.3: Abundance of the major (non-synthetic) isotopes of the Group 12 metals. Isotopes labeled with * are radioactive.

Many radioisotopes of zinc have been characterized. Zinc-65 that has a half-life of 244 days, is the most long-lived isotope, followed by ^{72}Zn with a half-life of 46.5 hours. The most common decay mode of an isotope of zinc with a mass number lower than 64 is electron capture, producing an isotope of copper, (5.1).



The most common decay mode of an isotope of zinc with mass number higher than 64 is beta decay ($\beta-$), which produces an isotope of gallium, (5.2).



Naturally occurring cadmium is composed of 8 isotopes. For two of them, natural radioactivity was observed, and three others are predicted to be radioactive but their decay is not observed, due to extremely long half-life times. The two natural radioactive isotopes are ^{113}Cd (half-life = 7.7×10^{15} years) and ^{116}Cd (half-life = 2.9×10^{19} years).

There are seven stable isotopes of mercury with the longest-lived radioisotopes being ^{194}Hg (half-life = 444 years) and ^{203}Hg (half-life = 47 days). ^{199}Hg and ^{201}Hg are the most often studied NMR-active nuclei, having spins of $\frac{1}{2}$ and $\frac{3}{2}$ respectively.

5.1.4 Properties

A summary of the physical properties of the Group 12 metals is given in Table 5.4. Because of the ns electron in the Group 12 metals are tightly bound, and hence relatively unavailable for metallic bonding, the metals are volatile with low boiling points, as compared to the Group 2 metals.

Element	Mp (°C)	Bp (°C)	Density (g/cm ³)
Zn	419.53	907	7.14
Cd	321.07	767	8.65
Hg	-38.83	356.73	13.534 (liquid)

Table 5.4: Selected physical properties of the Group 12 metals.

The most notable anomaly in the Group 12 metals is the low melting point of mercury compared to zinc and cadmium. In order to completely understand the reasons for mercury's low melting point quantum physics is required; however, the key point is that mercury has a unique electronic configuration, i.e., [Xe] 5d 6s. The stability of the 6s shell is due to the presence of a filled 4f shell, because an f shell poorly screens the nuclear charge that increases the attractive coulomb interaction of the 6s shell and the nucleus. Such a configuration strongly resists removal of an electron and as such mercury behaves similarly to noble gas elements, which form weakly bonded and thus easily melting solids (Figure 5.3).



Figure 5.3: Liquid mercury.

5.1.5 Industrial production

The vast majority (95%) of zinc is mined from of the zinc sulfide ores. The zinc is most often mixed with copper, lead, and iron. Zinc metal is produced by extraction, in which the ore is ground and then the minerals are separated from the gangue (commercially worthless mineral matter) by froth flotation (a process for selectively separating hydrophobic materials from hydrophilic). Roasting converts the zinc

sulfide concentrate produced to zinc oxide, (5.3). Reduction of the zinc oxide with carbon, (5.4), or carbon monoxide, (5.5), at 950 °C into the metal is followed by distillation of the metal. Since cadmium is a common impurity in zinc ores, it is most often isolated during the production of zinc. Cadmium is isolated from the zinc metal by vacuum distillation if the zinc is smelted, or cadmium sulfate is precipitated out of the electrolysis solution.



Mercury is extracted by heating cinnabar (HgS) in a current of air, (5.6), and condensing the vapor.



5.2 Group 12 Chalcogenides

5.2.1 Cadmium Chalcogenide Nanoparticles²

The most studied non-oxide semiconductors are cadmium chalcogenides (CdE , with $E = \text{sulfide, selenide}$ and telluride). CdE nanocrystals were probably the first material used to demonstrate quantum size effects corresponding to a change in the electronic structure with size, i.e., the increase of the band gap energy with the decrease in size of particles (Figure 5.4). These semiconductors nanocrystals are commonly synthesized by thermal decomposition of an organometallic precursor dissolved in an anhydrous solvent containing the source of chalcogenide and a stabilizing material (polymer or capping ligand). Stabilizing molecules bound to the surface of particles control their growth and prevent particle aggregation.

²This content is available online at <<http://cnx.org/content/m22374/1.4/>>.



Figure 5.4: Picture of cadmium selenide (CdSe) quantum dots, dissolved in toluene, fluorescing brightly, as they are exposed to an ultraviolet lamp, in three noticeable different colors (blue ~ 481 nm, green ~ 520 nm, and orange ~ 612 nm) due to the quantum dots' bandgap (and thus the wavelength of emitted light) depends strongly on the particle size; the smaller the dot, the shorter the emitted wavelength of light. The "blue" quantum dots have the smallest particle size, the "green" dots are slightly larger, and the "orange" dots are the largest.

Although cadmium chalcogenides are the most studies semiconducting nanoparticles, the methodology for the formation of semiconducting nanoparticles was first demonstrated independently for InP and GaAs, e.g., (5.7). This method has been adapted for a range of semiconductor nanoparticles.



In the case of CdE, dimethylcadmium $\text{Cd}(\text{CH}_3)_2$ is used as a cadmium source and bis(trimethylsilyl)sulfide, $(\text{Me}_3\text{Si})_2\text{S}$, trioctylphosphine selenide or telluride (TOPSe, TOPTe) serve as sources of selenide in tri-octylphosphine oxide (TOPO) used as solvent and capping molecule. The mixture is heated at 230-260 °C over a few hours while modulating the temperature in response to changes in the size distribution as estimated from the absorption spectra of aliquots removed at regular intervals. These particles, capped with TOP/TOPO molecules, are non-aggregated (Figure 5.5) and easily dispersible in organic solvents forming optically clear dispersions. When similar syntheses are performed in the presence of surfactant, strongly anisotropic nanoparticles are obtained, e.g., rod-shaped CdSe nanoparticles can be obtained.

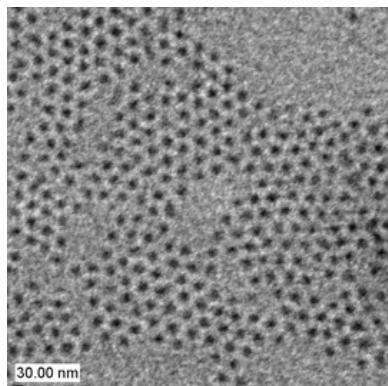


Figure 5.5: TEM image of CdSe nanoparticles.

Because $\text{Cd}(\text{CH}_3)_2$ is extremely toxic, pyrophoric and explosive at elevated temperature, other Cd sources have been used. CdO appears to be an interesting precursor. CdO powder dissolves in TOPO and HPA or TDPA (tetradecylphosphonic acid) at about 300°C giving a colorless homogeneous solution. By introducing selenium or tellurium dissolved in TOP, nanocrystals grow to the desired size.

Nanorods of CdSe or CdTe can also be produced by using a greater initial concentration of cadmium as compared to reactions for nanoparticles. This approach has been successfully applied for synthesis of numerous other metal chalcogenides including ZnS, ZnSe, and $\text{Zn}_{1-x}\text{Cd}_x\text{S}$. Similar procedures enable the formation of MnS, PdS, NiS, Cu₂S nanoparticles, nano rods, and nano disks.

5.2.1.1 Bibliography

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5.3 Organometallic Chemistry

5.3.1 Organometallic Chemistry of Zinc³

The first dialkyl zinc derivatives, Me_2Zn and Et_2Zn , were prepared in 1848 by Edward Franklin (Figure 5.6). He also prepared the monoalkyl derivatives, RZnX .

³This content is available online at <<http://cnx.org/content/m32446/1.2/>>.

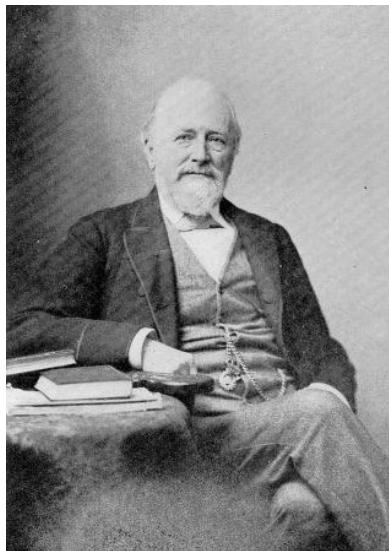
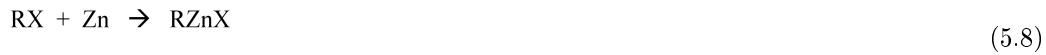


Figure 5.6: British chemist Sir Edward Franklin FRS (1825 –1899).

Initially alkyl zinc compounds were used in organic synthesis, however, their use diminished significantly once Grignard reagents had been discovered. Little further was investigated of their chemistry until their use in the growth of electronic materials developed in the 1980's.

5.3.1.1 RZnX

The monoalkyl derivatives are not widely used, but were historically the first to be prepared, (5.8).



While the iodide derivatives can be isolated as unsolvated derivatives, the chloride and bromides need to be prepared in the presence of dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). Alternative methods of synthesis involve the reaction with a Grignard reagent, (5.9), or electrochemical synthesis with a zinc electrode.



In the solid state RZnI exists as cage oligomers or polymeric chain structures. These structures are broken by the addition of strong Lewis bases to form Lewis acid-base complexes. In solution there exists a Schlenk equilibrium, (5.10), whose presence has been determined by IR and Raman spectroscopy (Table 5.5).

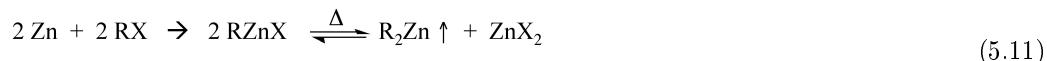


Stretch	IR (cm^{-1})	Raman (cm^{-1})
symmetric C-Zn-C	Not observed	477
asymmetric C-Zn-C	551	Not observed
C-Zn-I	510	510

Table 5.5: IR and Raman spectroscopic characterization of the components of the Schlenk equilibrium, (5.10).

5.3.1.2 R_2Zn

Dialkyl zinc compounds are prepared via the monoalkyl derivatives, (5.11). The Schlenk equilibrium is shifted at high temperatures by the distillation of the volatile R_2Zn derivative. The zinc is usually alloyed with copper (10%) to improve the reaction rate.



Alternative preparation methods include the reaction of ZnX_2 with a Grignard, (5.12), or by metal-metal exchange, (5.13).



5.3.1.3 Bibliography

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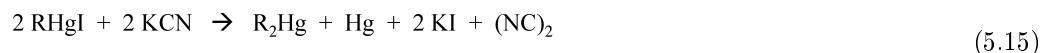
5.3.2 Organomercury Compounds⁴

5.3.2.1 Synthesis

The most common routes to organomercury compounds involve the direct reaction of mercury with an alkyl iodide, (5.14), to form the mercury analog of a Grignard reagent.

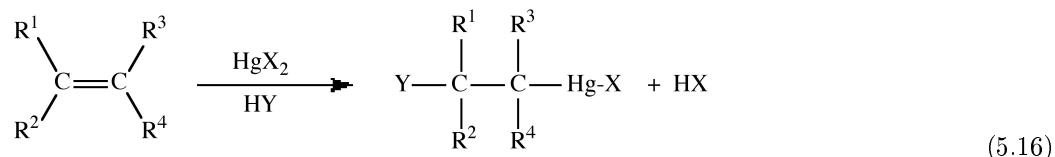


The subsequent reaction of RHgI with potassium cyanide yields the appropriate dialkyl mercury derivative, (5.15).



5.3.2.1.1 Solvomercuration

The general process of solvomercuration involves the addition of HgX_2 across an alkene double (or alkyne triple) bond in the presence of a solvent, (5.16). Solvomercuration applies where HY , from (5.16), are part of the solvent system, e.g., in water the process can be described as hydroxymercuration.

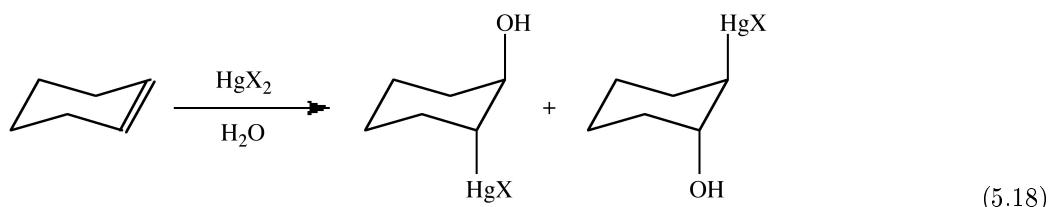


⁴This content is available online at <<http://cnx.org/content/m32520/1.3/>>.

The addition to the alkene occurs with Markovnikoff addition, i.e., through the formation of the most stable carbonium ion resulting with the mercury adding to the less substituted carbon. The Hg-C bond can be cleaved by the addition of NaBH_4 to yield the C-H bond. It is common to employ mercury acetate, $\text{Hg}(\text{OAc})_2$ ($\text{OAc} = \text{O}_2\text{CCH}_3$), with subsequent reaction with NaCl or NaI to form the halide, rather than the mercury halide directly. However, the acetate can also act as a nucleophile resulting in a mixture of products. The order of reactivity for alkenes follows the trend:



This is due to a combination of steric and electronic effects. The addition occurs in a *trans/anti* fashion, (5.18).



Mercury(II) halides dissociate in polar solvents, (5.19), and this species is commonly associated with the initial reaction step.



The mechanism of solvomercuration is best described by the reaction shown in Figure 5.7.

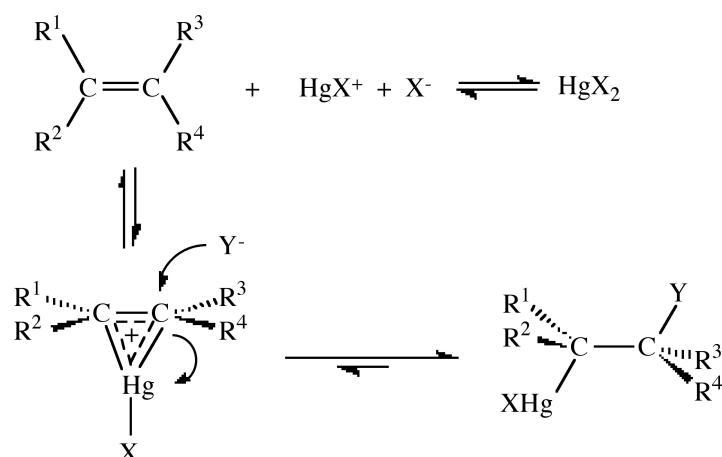


Figure 5.7: Mechanism of solvomercuration.

Evidence for the mechanism is twofold:

1. The addition is exclusively *trans*.
2. No rearrangement is observed even for ${}^t\text{Bu}(\text{H})\text{C=C(H)}{}^t\text{Bu}$ whose carbonium ion is known to undergo rearrangement.

Isotope studies indicate that the C-O bond formation is present in the transition state (Figure 5.8). The mercury bridge in the transition state may not be symmetrical, but the structure is similar to the addition of Br^+ and AuX^+ to alkenes.

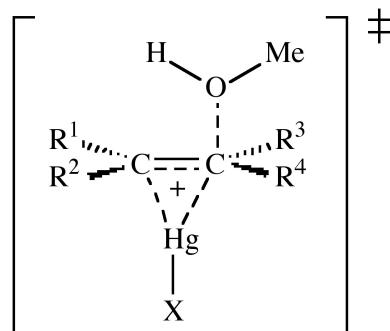


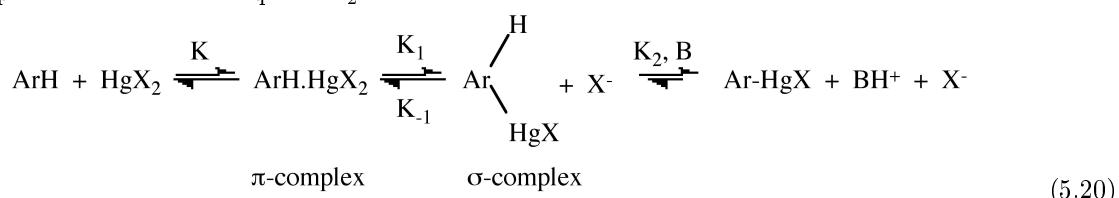
Figure 5.8: Proposed transition state for the solvomercuration reaction where the solvent is methanol.

The actual reaction was originally carried out with Hg(OAc)_2 in benzene at 110 °C for several hours in acetic acid solution. It was found that the reaction was catalyzed by the presence of HClO_4 , H_2SO_4 , and HNO_3 , which were found to replace the acetate ion. The reaction rate is also increased by 690,000 times by the use of $\text{Hg(O}_2\text{CCF}_3)_2$ in HO_2CCF_3 .

The solvomercuration of alkynes gives alkenylmercury compounds, but the reaction is more sluggish than for the reaction with alkenes, and the product is always the *trans* isomer.

5.3.2.1.2 Mercuration of aromatic compounds

Mercuration is an electrophilic aromatic substitution reaction that is possible for most $2n+2$ π -electron species, (5.20). Evidence for the π -complex intermediate is indicated by UV spectroscopy, which shows an increase in the region 280 – 320 nm for the reaction of aromatic compounds with $\text{Hg(O}_2\text{CCF}_3)_2$ in HO_2CCF_3 . The σ -complex has detected in liquid SO_2 .



As a preparative method mercuration suffers from lack of selectivity, including an isomerization from *para* substitution at low temperature to *meta* substitution at high temperatures.

5.3.2.2 Structure

Dialkyl mercury compounds, R_2Hg , are generally air stable and show little Lewis acid behavior. They are monomeric colorless liquids or low melting solids, e.g., $\text{Bp} = 92.5$ °C for Me_2Hg . No solubility is observed in water, except for $(\text{F}_3\text{C})_2\text{Hg}$, (5.21).



The hybridization at mercury involves the 6s and 6p orbitals; however, the 5d may be involved. X-ray crystal structures for both R_2Hg and $RHgX$ show linear structures. In general R_2Hg compounds are very weak Lewis acids, but adducts are formed if the alkyl group is sufficiently electron withdrawing, e.g., $(C_6F_5)_2Hg$. The geometry of the Lewis acid-base complex is not triangular as predicted from VSEPR theory, but a *T*-shape. The distortion from a linear C-Hg-C unit is minor. For example, in $(C_6F_5)_2Hg$ the C-Hg-C angle is 176.2° , while in $[(C_6F_5)_2Hg]_2(\text{diars})$, where diars = $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (Figure 5.9), the same angle is 173° . Furthermore, the donor atom-Hg bond distance (e.g., As-Hg = 3.4 \AA) is only slightly shorter than the sum of the van der Waal radii (e.g., 3.5 \AA).

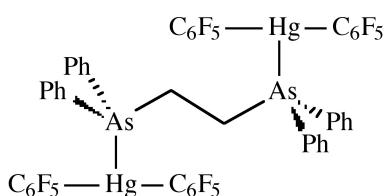


Figure 5.9: The structure of $[(C_6F_5)_2Hg]_2(\text{diars})$.

5.3.2.3 Bibliography

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5.4 The Myth, Reality, and History of Mercury Toxicity⁵

Mercury has a reputation for being a dangerous element, but is its reputation deserved? Given the large-scale use of mercury today it is important to understand the risks and issues related to mercury exposure. Nowhere is this now important than with the use of mercury for small low energy fluorescent lights (Figure 5.10) that are being advocated by everyone from the electricity companies to Greenpeace.

⁵This content is available online at <<http://cnx.org/content/m32333/1.5/>>.



Figure 5.10: An example of a modern low energy mercury vapor fluorescent light.

When considering the issue of mercury toxicity it is important to separate the effects of mercury metal (as a liquid or vapor) from the compounds of mercury.

5.4.1 Mercury metal

It was found very early on that people who worked with mercury, in mining for example, had very bad health. Other jobs that exposed people to mercury were mirror makers and hatters (people who manufactured hats). The problems in this latter occupation will forever live on with one of the central characters in Lewis Carroll's *Alice's Adventures in Wonderland*; the Mad Hatter.

Hats were made from felt, which is a non-woven textile of animal hair. Wool interlocks naturally due to the surface texture of the individual hairs, but rabbit and beaver have to be artificially roughened. This process was usually accomplished with nitric acid (HNO_3). It was found that if mercury was added to the nitric acid, a better quality of felt was produced. Unfortunately, when the felt was dried a fine dust was formed containing mercury. The hatters who shaped the felt inhaled large quantities of this dust were found to suffer from excessive salivation, erethism (presenting with excessive shyness, timidity and social phobia), and shaking of the limbs, which became known as *hatter's shakes*. The madness that was observed is the derivation of the phrase "mad as a hatter".

NOTE: It is interesting that while Carroll's Mad Hatter is mad, he does not show the classic symptoms of mercury poisoning. In particular he can be in no way described as shy!

Hatters were not the only people that mercury caused a problem for. Chemists doing research using large quantities of mercury were also affected. They were given to violent headaches, tremors of the hands, "socially troublesome inflammation of the bladder", loss of memory, and slow mental processes. In 1926 Alfred Stock (Figure 5.11) and his research group all suffered from symptoms. However, when the lab was cleaned of mercury the symptoms went away.



Figure 5.11: German chemist Alfred Stock (1876 –1946).

Many other notable scientists have also suffered from mercury poisoning. Faraday (Figure 5.12), Pascal (Figure 5.13), and most probably Sir Isaac Newton (Figure 5.14) were affected. As part of his research studies, Newton boiled several pounds of mercury a day just before his period of insanity between 1692 and 1693. It is likely that the mercury vapor was the cause of his malady. However, in each case, the symptoms (and insanity) abated once the source of mercury was removed.



Figure 5.12: An engraving by John Cochran of English chemist and physicist Michael Faraday, FRS (1791 –1867).



Figure 5.13: French mathematician, physicist, and religious philosopher Blaise Pascal (1623 – 1662).



Figure 5.14: English physicist, mathematician, astronomer, natural philosopher, alchemist, and theologian Sir Isaac Newton FRS (1643 –1727). Portrait by Godfrey Kneller.

NOTE: It is important to remember that in all the cases described above it is the inhalation of the mercury vapor that was the cause of the trouble. Solid alloys of mercury such as those found in dental fillings have never been shown to cause any medical issues directly. Despite this the US banned the use of Cu/Hg dental amalgams until 1850! More recently, it has been suggested that dentists are exposed at higher levels during the placing and removal of fillings. Dentists as a group have higher mercury levels than those associated with people with amalgam restorations, but experience no increase in disease or death rates, and in fact tend to be healthier than the general population.

Although elemental mercury was clearly toxic, this did not stop its use in pharmacy for hundreds of years. In the 1500's mercury was used in the treatment (albeit ineffective) of syphilis. Syphilis was a new disease in Europe; it had been brought back from America by Columbus' sailors, and was promptly spread through Europe by the French army, amongst others! Syphilis was much more fatal and had more dramatic symptoms than today.

Initially mercury was used as an ointment, but the patients often got worse. Then there was *the tub*, which was a mercury vapor bath, and even calomel (Hg_2Cl_2) was used, but with little effect. These treatments were used for over four centuries, but none provided a cure, despite claims at the time. For example, John Hunter, a doctor who gave himself syphilis by mistake (!) claimed he had been cured, but he actually died of a heart attack during an argument, so it is unlikely the mercury worked. Despite this it became known that "a night with Venus results in a lifetime with Mercury".

The reasons that mercury was thought erroneously to cure syphilis are twofold:

1. Until 1906 it was difficult to diagnose syphilis. It was often confused with gonorrhea, and therefore it is likely that some people did not have the far more deadly syphilis.
2. Syphilis occurs in three phases, each with remission between the phases. The period of remission between secondary and tertiary phases can be two to three years, and therefore it may appear that a cure is found. Especially as many patients (like John Hunter) died other deaths during this remission phase.

The prevalent use of mercury and its presence in many cadavers, led some doctors to assume that mercury was a natural part of the body. It was not just humans that were treated with mercury, cattle were also treated, and one druggist sold 25 tons of mercury to a single farmer in one year!

The density of mercury and its liquid state at room temperature led to another unusual application that was somewhat more successful, although equally dangerous: constipation. In medical texts of the time it was noted that "mercury is given in the disease called *Miserere*, unto two or three pounds, and is voided again by siege to the same weight; it is better to take a great deal of it than a little, because a small quantity might be apt to stop in the circumvolutions of the guts, and if some acid humors should happen to join with it, a *sublimate corrosive* would be made; but when a large quantity of it is taken, there's no need to fearing this accident, because it passes through by its own weight."

It is interesting that the mention of the *corrosive sublimate*; this is in fact mercury(II) dichloride ($HgCl_2$) which unlike mercury(I) chloride (Hg_2Cl_2), is a very violent poison. Death is caused by renal failure. So while there is no evidence for elemental mercury itself causing fatalities, its compounds are another matter to be considered.

5.4.2 Organomercury compounds

In 1953 it was noted that the fishing village of Minamata in Japan had an epidemic in which a large number of people died. Initial thoughts of either an infectious disease or malnutrition were discounted; then it was found that the fish eaten by the villagers was highly contaminated by mercury.

It was found that the mercury came from the Chisso Corporation chemical plant that made acetaldehyde from acetylene using a mercury catalyst. The plant was losing 1 Kg of mercury metal for every ton of acetaldehyde being produced. As a consequence it was originally assumed that the poisoning of the village was due to inorganic mercury. Based upon prior incidents, an obvious response was to ban consumption of all fish and shellfish. As a consequence no new cases were reported, however, people already effected continued to die. This was unlike any previous mercury poisoning.

Further analysis showed small quantities of water soluble methyl mercury ($MeHg^+$) was present and sequestered by the shellfish to give $MeHgSMe$. While the lethal effects of organomercury compounds were known, the source of the methyl mercury was a mystery. A group of Swedish researchers showed that the bacterial action in river sediment or rotting fish converted inorganic mercury to either volatile Me_2Hg or water soluble $MeHg^+$. With this discovery, it was understood how the anaerobic mud of the estuary near Minamata could perform this methylation.

Of course Minamata was not the first report or an organomercury compound, but it was the first time that it was shown that mercury metal could be converted to a highly toxic organometallic derivative in the environment. The hazardous nature of organomercurials was found almost as soon as the first compounds were reported!

While working in Bunsen's research group in Marburg, Edward Franklin (Figure 5.15) discovered the synthesis of the zinc analog of a Grignard reagent, (5.22). Subsequently, in 1851 Franklin moved to Owens College in Manchester where he extended his work to mercury, (5.23). In his publication he noted that these organomercury compounds had a "nauseous taste", but didn't realize they were toxic.

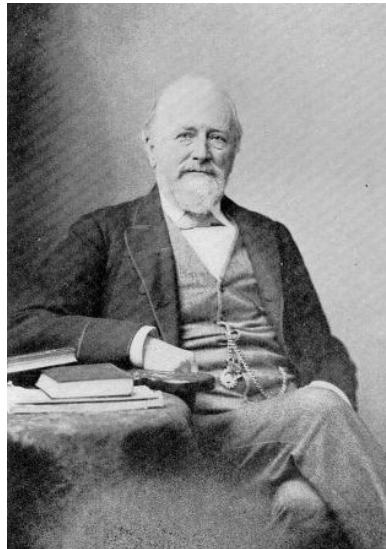


Figure 5.15: British chemist Sir Edward Franklin FRS (1825 – 1899).

In 1858 George Buckton (Figure 5.16) working at the then Royal College of Chemistry (now Imperial College) reported the synthesis of dimethyl mercury, (5.24), as a volatile liquid.

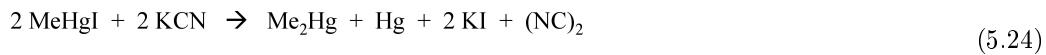




Figure 5.16: British chemist George Buckton (1818 - 1905).

When Frankland moved his research to St Bartholomew's Hospital ("Barts") London he started looking into the chemistry of R_2Hg with an assistant called Bill Odling in collaboration with Dr Carl Ulrich.

Ulrich died in 1865 as a consequence of exposure to Me_2Hg . In his own statement, he had inhaled a large quantity of the volatile compound without having taken the proper precautions. The following day "his countenance had attained a dull, anxious, and confused expression" and he was admitted to the hospital in a weak condition on 3rd February. On the 9th he became noisy and had to be put under mechanical restraint. The next day his breath and body began to smell offensively and he was in a coma. He would rise from the coma periodically to utter incoherent howls. He died on the 14th of February.

A technician from the same research group (who is only identified as 'T. C.') was also admitted to the hospital on 28th March of the same year. His symptoms were initially milder than Ulrich's, but soon developed. By that summer he was completely demented, with no control over his body functions. He stayed in this state for many months, only dying on 7th April 1866. Records indicate that a third assistant was also taken ill, but there was no further mention of him, so it is unknown if he died.

5.4.3 Summary and the “green” future

Metallic mercury causes severe symptoms, but all records show that if the patient is removed from the source they recover. Thus, short term exposure to metallic mercury, while dangerous, is not fatal if proper precautions are taken. In contrast, mercury compounds offer different risks. As a general rule, inorganic mercury(I) compounds are far less toxic than their mercury(II) analogs, however, all should be treated with care.

Where mercury compounds offer the greatest risk of fatality is their organometallic derivatives. There is no known cure for exposure to even modest doses of organomercury compounds. Furthermore, the ability of elemental mercury to be transformed into water-soluble organomercury compounds such as $MeHg^+$, offers a future threat to public health.

The new generation of low energy consumption light bulbs contain mercury vapor. While they last longer than a traditional tungsten filament light bulb (Figure 5.10), they do have a lifetime. The presence of mercury means that they should be disposed-off separately from household waste to ensure that when the glass is broken the mercury is not released; however, this is unlikely. Most will be disposed off along

with household waste which may be subsequently land filled. The lesson from Minamata should be that the bacterial action under anaerobic condition allows for the formation of water soluble MeHg^+ , that can diffuse into the water table. Although the amount of mercury in each bulb is very small, the highly lethal nature (low LD_{50}) of orgnaomercury compounds should be considered in efforts to conserve energy by the use of the low energy light bulbs. At the very minimum protocols for their efficient disposal and recycling should be in place.

5.4.4 Bibliography

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