Skills to Develop

In this lecture you will learn the following

- Organoaresnic and organoantimony compounds.
- Preparation and reactivity of pentavalent As and Sb compounds.

Organic chemistry of non-metal phosphorus, metalloids such as arsenic and antimony along with metallic element bismuth is termed as organoelement chemistry. The importance given to organoarsenic compounds earlier due to their medicinal values was waded out after antibiotics were discovered and also their carcinogenic and toxic properties were revealed. Also, the synthetically important organometallic compounds of group 13 and 14 masked the growth of group 15 elements. However, the organoelement compounds of phosphorus, arsenic and antimony find usefulness as ligands in transition metal chemistry due to their \( \sigma \)-donor and \( \pi \)-acceptor abilities which can be readily tuned by simply changing the substituents. These donor properties are very useful in tuning them as ligands to make suitable metal complexes for metal mediated homogeneous catalysis. Although organoelement compounds can be formed in both +3 (trivalent and tricoordinated) and +5 (pentavalent and tetra or pentacoordinated) oxidation states, trivalent compounds are important in coordination chemistry.

For organoelement compounds of group 15, the energy of E—C bond decreases in the order, \( E = P > As > Sb > Bi \), and in the same sequence E—C bond polarity increases.

Organometallic compounds of As(V) and Sb(V)

Due to the strong oxidizing nature of pentahalides, the direct alkylation or arylation to generate \( ER_5 \) is not feasible, but can be prepared in two steps.

A few representative methods of preparation are given below:

\[
\begin{align*}
\text{Me}_3\text{As} + \text{Cl}_2 & \rightarrow \text{Me}_3\text{AsCl}_2 \\
\text{Me}_3\text{AsCl}_2 + \text{MeLi} & \rightarrow \text{Me}_4\text{As} \\
\text{Ph}_3\text{Sb} + \text{PhI} & \rightarrow \text{Ph}_4\text{SbI} \\
\text{Ph}_3\text{Sb} & \rightarrow \text{Ph}_3\text{Sb} \\
\text{Ph}_3\text{Bi} + \text{SO}_2\text{Cl}_2 & \rightarrow \text{Ph}_3\text{BiCl}_2 \\
\text{Ph}_3\text{BiCl}_2 & \rightarrow \text{Ph}_3\text{Bi}
\end{align*}
\]

Structures and properties

Pentaalkyl or pentaaryl derivatives are moderately thermally stable. On heating above 100°C, they form trivalent compounds as shown below:
Reaction with water,

\[
\begin{align*}
\text{Me}_5\text{As} + \text{H}_2\text{O} & \rightarrow \text{Me}_4\text{AsOH} + \text{MeH} \\
\text{Ph}_5\text{Sb} + \text{Ph} \rightarrow \text{Ph}_3\text{Sb} + \text{Ph} \rightarrow \text{Ph}_3\text{Sb} + \text{Ph} 
\end{align*}
\]

Pentavalent compounds readily form “tetrahedral onium” cations and “octahedral and hexacoordinatged ate” anions.

\[
\begin{align*}
\text{Ph}_3\text{E} & + \text{BPh}_3 \rightarrow [\text{Ph}_4\text{E}][\text{BPh}_4] \\
\text{Ph}_3\text{E} & + \text{LiPh} \rightarrow \text{Li}\{\text{EPbSb}\}
\end{align*}
\]

In solid state, Ph₅As adopts trigonal bipyramidal geometry, whereas Ph₅Sb prefers square based pyramidal geometry although the energy difference between the two is marginal.

The salts of the type \([\text{R}_4\text{E}]^+\) adopt tetrahedral geometry, whereas hexacoordinated anions \([\text{R}_6\text{E}]^-\) assume octahedral geometry.

Mixed organo-halo compounds of the type \(\text{R}_n\text{EX}_{5-n}\) adopt often dimeric structures due to the presence of lone pairs of electrons on \(\text{X}\) which can readily coordinate to the second molecule. The following structural types can be anticipated.

The thermal stability of \(\text{R}_n\text{EX}_{5-n}\) decreases with decreasing ‘\(n\)’. Thermal reactions are essentially the reverse reactions of addition reactions used in the preparation of \(\text{R}_5\text{E}\).
Organometallic compounds of As(III) and Sb(III)

In this lecture you will learn the following

• Preparation of trivalent compounds.
• Mono and bis derivatives.
• Reaction of organo arsenic and antimony compounds.
• Structural features of organolead compounds.

Organometallic compound of As(III) and Sb(III).

Direct synthesis

Mono- derivatives

\[
\begin{align*}
2\text{As} + 3\text{MeBr} & \xrightarrow{\Delta T} \text{Me}_2\text{AsBr} + \text{MeAsBr}_2 \\
\text{Me}_2\text{AsBr} + \text{PhLi} & \rightarrow \text{Me}_2\text{AsPh} \\
\text{MeAsBr}_2 + 2\text{PhLi} & \rightarrow \text{MeAsPh}_2 \\
\text{EX}_3 + 3\text{RMgX} & \rightarrow \text{R}_3\text{E} + 3\text{MgX}_2 \\
\text{EX}_3 + 3\text{RLi} & \rightarrow \text{R}_3\text{E} + 3\text{LiX}
\end{align*}
\]

Direct synthesis (contd..)

Bis derivatives:
Reactions of trialkyl derivatives, R₃E

The transition metal chemistry of R₃E, phosphines, arsines or stibines has been extensively studied because of their distinct donor and acceptor properties. Among them, the phosphines or tertiary phosphines (R₃P) are the most valuable ligands in metal mediated homogeneous catalysis. Interestingly, the steric and electronic properties can be readily tuned by changing the substituents on phosphorus atoms. Chapter 16 is fully dedicated to the chemistry of phosphines.

Properties

Trialkyl derivatives are highly air-sensitive liquids with low boiling points and some of them are even pyrophoric. Triphenyl derivatives are solids at room temperature and are moderately stable and oxidizing agents such as KMnO₄, H₂O₂ or TMNO are needed for oxidation to form Ph₃E=O.

Cyclic and acyclic derivatives containing E—E bonds

**E—E single bonds:**

The E—E bond energies suggest that they do not have greater stability and the stability decreases down the group. The simplest molecules include Ph₂P—PPh₂, Me₂As—AsMe₂ prepared by coupling reactions:

\[
\text{Me}_2\text{AsH} + \text{Me}_2\text{AsCl} \xrightarrow{-\text{HCl}} \text{Me}_2\text{As} - \text{AsMe}_2 \\
2\text{Ph}_2\text{BiCl} \xrightarrow{\text{Na}, \text{NH}_3} \text{Ph}_2\text{Bi} - \text{BiPh}_2
\]
The weakness of E—E bonds accounts for many interesting reactions and a few of such reactions are listed below:

Cyclic and polycyclic derivatives can be prepared by employing any of the following methods:

Problems

1. Confirm that the octahedral structure of [Ph₆Bi]⁺ is consistent with VSEPR theory.

   Solution:
   Octahedral similar to PF₆⁻
   5 (Bi valence electrons) + 6 (each Ph) + 1 (-ve charge) = 12 electrons
   i.e. six pairs, octahedral geometry

2. Comment on the stability of BiMe₃ and Al₂(⁰Bu)₆ with respect to their thermal decomposition and give chemical equations for their decomposition.

   Solution:
   Similar to other heavy p-block elements, Bi—C bonds are weak and readily undergo homolytic cleavage. The resulting methyl radicals will react with other radicals or form ethane

   \[
   2 \text{BiMe}_3 \rightarrow 2\text{Bi} + 3 \text{CH}_3\cdot\text{CH}_3
   \]

   The Al₂(⁰Bu)₆ dimer readily dissociates. At elevated temperature dissociation is followed by β-hydrogen elimination. This type of elimination is common for organometallic compounds that have alkyl groups with β-hydrogens, can form stable M—H bonds, and can provide a coordination site on the central metal.

   The decomposition reaction is:
Problems: (contd..)

3. Using a suitable Grignard reagent, how would you prepare (i) MeC(Et)(OH)Ph; (ii) AsPh₃.

Solution:

1. Add a Grignard reagent to a C=O bond, then acidify.

   Several possibilities, e.g.
   
   Me-C(O)-Et + PhMgBr → Me-C(OMgBr)(Et)(Ph) → MeC(Et)(OH)Ph or Me-C(O)-Ph + EtMgBr → etc

2. AsCl₃ + 3PhMgBr → AsPh₃ + 3MgBrCl.

3. This Module focuses on Main Group Organometallic Chemistry will look at some "simple" methyl and ethyl compounds; (Me₂As)₂, Me₃As, Me₂Hg and Et₄Pb.

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**Organoarsenic Chemistry**

"Cadet's fuming liquid"

The French pharmacist-chemist, Louis-Claude Cadet de Gassicourt prepared what became known as "Cadet's fuming liquid" in 1757. The reaction involved heating 2 ounces of arsenious oxide with 2 ounces of potassium acetate.

\[As_2O_3 + 4 CH_3COOK \rightarrow As_2(CH_3)_4O + 4 K_2CO_3 + CO_2 \rightarrow As_2(CH_3)_4\]

gives cacodyl oxide which disproportionates to produce among other things cacodyl, As₂(CH₃)₄.
He noted that:

"a slightly colored liquid of an extremely penetrating garlic odor distills and then a red-brown liquid which fills the receiver with thick fumes".

All of the early studies of Cadet's fuming liquid were qualitative in nature, made difficult by the liquid's horrible stench and inflammability, and it was not until the investigations of Robert Wilhelm Bunsen during 1837-1843 that more useful information concerning Cadet's fuming liquid became available. The history of studies on this mixture was reviewed in 2001 [Ref 3.]

Bunsen opted for a large-scale preparation, despite the fact that he was aware of the repulsive and dangerous nature of the expected products. Starting out with one kilogram of a 1:1 by weight As$_2$O$_3$/KOOCCH$_3$ mixture in a glass retort, he heated it very slowly to red heat in a sand bath. As Cadet had reported, two liquid layers and a solid phase collected in the receiver. Bunsen reported that he obtained ~150 g of the red-brown liquid.

In 1841, Berzelius suggested to Bunsen that the name for the liquid be called "kakodyl" from the Greek meaning "stinking", the English spelling of this was cacodyl.

"Accidents with cacodyl compounds could have serious consequences. During his study of cacodyl cyanide, (CH$_3$)$_2$AsCN, prepared by reaction of 'cacodyl oxide' with a concentrated aqueous solution of mercuric cyanide, an explosion cost Bunsen the partial sight of his right eye and, as Roscoe reports, 'Bunsen was nearly poisoned, lying for days between life and death.' Bunsen recovered and completed his study of cacodyl cyanide, a most unpleasant compound. After distillation of the 'cacodyl oxide'/Hg(CN)$_2$ reaction mixture, the cacodyl cyanide formed beautiful, prismatic crystals underneath the water layer. These were quite volatile (mp 32.5 °C). They were dried by pressing them between sheets of blotting paper. Bunsen noted that it is absolutely necessary to carry out this operation in the open air while breathing through a long glass tube that extends to fresh air far beyond the volatile crystals. And well might this compound be avoided! Bunsen reported that the vapour from 1 grain (0.0648 g) of cacodyl cyanide in a room produces sudden numbness of the hands and feet, and dizziness and insensitivity to the point of unconsciousness. The tongue becomes covered with a black coating. These effects, however, are only temporary, with no lasting problems. (Bunsen, it may be noted, lived to the ripe old age of 88.)" Ref 3.

Seventy years after its discovery, the question of the composition of Cadet's fuming liquid was addressed by Valeur and Gailliot by means of its fractional distillation under an atmosphere of CO$_2$. Valeur, A.; Gailliot, P. C. R. Acad. Sci. 1927, 185, 956.

<table>
<thead>
<tr>
<th>Composition of Cadet's fuming liquid (1927)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>(CH$_3$)$_2$As</td>
</tr>
<tr>
<td>(CH$_3$)$_2$AsOAs(CH$_3$)$_2$ &quot;cacodyl oxide&quot;</td>
</tr>
</tbody>
</table>
The use of Cadet's fuming liquid was considered for use in chemical warfare during both WWI and WWII and plants in both Germany and the USA were said to have developed processes for large-scale production. During WWI an organoarsenic compound was used (Lewisite) but not Cadet's liquid.

The exact composition of Cadet's fuming liquid is still unclear but with today's array of sophisticated spectroscopic instruments it should be possible to find a definitive answer. The problems of toxicity etc. are no longer an insurmountable problem given the handling techniques and glassware that were developed beginning with the experimental work of the early synthetic chemists like Bunsen and Schlenk.

"Gosio gas"

Another "simple" methyl derivative, Me₃As, has a long history as well. In 1893 the Italian physician Bartolomeo Gosio published his results on "Gosio gas" that was subsequently shown to contain trimethylarsine. Under wet conditions, the mould Scopulariopsis brevicaulis produces significant amounts of methyl arsines via methylation of arsenic-containing inorganic pigments, especially Paris green/Schweinfurt-green("copper arsenite plus copper acetate") and Scheele's Green ("copper arsenite") which were once used in indoor wallpapers. In other cases the arsenic had been added to the wallpaper paste to discourage rodents and insects. Gosio gas was responsible for a number of deaths, and the air in the buildings in which it was being produced had a characteristic garlic-like odour. Gosio established the source of the problem and isolated some of the moulds capable of metabolizing inorganic arsenicals. Pietro Biginelli aspirated the gas from cultures through acidified (HCl) mercuric chloride solution. On the basis of an analysis of the precipitate so obtained, he incorrectly identified the gas as diethylarsine (Et₂AsH). Nonetheless, this was a considerable achievement and established the methodology that Frederick Challenger was to use some 30 years later in his classic studies, beginning with the positive identification of the mould metabolite as trimethylarsine.

Newer studies suggest that trimethyarsine has a lower toxicity than originally thought and may not account for the death and the severe health problems observed in the 19th century which may have arisen due to volatile organics produced from moulds (now linked to what has been called "sick-building syndrome")

Lead arsenate dust from a painted ceiling was the source of the arsenic that caused health problems for Clare Boothe Luce when she was living in Rome as U.S. Ambassador in 1954. No mould action was implicated. One theory was that a washing machine in an upstairs room caused vibrations that dislodged some arsenic containing paint from the stucco decorating her bedroom ceiling!
Me₃As

AsMe₃ is a pyramidal molecule as predicted by VSEPR theory. The As-C distances average 151.9 nm, and the C-As-C angles are 91.83°.

References
1. Organoarsenic and trimethylarsine on Wikipedia.
2. Scheele's Green killed Napoleon?
4. Toxicity of Me₃As: Urban Myth?

Methylmercury

The usual method of ingestion of a metal into the body is:
1. Orally - the Gastrointestinal Tract
2. via the lungs - the Respiratory Tract

a) Orally - (mouth, stomach, small intestine).

Food digestion begins in the mouth where saliva containing the enzyme amylase breaks down starch to lower sugars. Most digestion occurs in the stomach in the presence of HCl (pH ~1.6 i.e. 0.17M HCl). In the case of mercury it is quite readily absorbed through the stomach since reaction of mercury salts with HCl produces HgCl₂. This neutral covalent molecule (solubility in H₂O 0.5 g/100 mL but 8g/100 mL in ethanol) is absorbed far better than most inorganic ions and this no doubt contributes to its high toxicity.

b) Respiratory tract (nose, lungs). This is usually unimportant for most metals but in some cases it can be more efficient that via the gastrointestinal tract. For example, lead where 50% of Pb in air can be absorbed but only 5-10% via the gastrointestinal tract. Volatile dimethyl mercury is another case for concern.
Mercury is 62nd in terms of natural abundance and is found everywhere, usually as the mineral cinnabar, HgS, although 30 minerals containing Hg are known. The oxidation states are Hg(0), Hg(I) and Hg(II), where Hg(I) has been shown to exist as Hg$_2^{2+}$.

The three Hg species are related by the disproportionation:

Hg$_2^{2+}$ → Hg$^0$ + Hg$^{2+}$ $E^o = -0.131$ V

or K= 6 x 10$^{-3}$

In addition:

Hg$^{2+}$/Hg $E^o = 0.789$ V

Hg$^{2+}$/Hg $E^o = 0.854$ V
This means that to oxidise Hg to \( \text{Hg}_2^{2+} \) an oxidising agent with potential > 0.789 V is required, but very importantly < 0.854 V, otherwise oxidation to Hg\(^{2+} \) will occur. There are no common oxidants that fit this arrangement so if any reaction occurs the product will be Hg\(^{2+} \). The equilibrium constant of \( 6 \times 10^{-3} \) shows that when Hg(I) is formed it is moderately stable, however any agent that reduces the Hg(II) concentration automatically drives the reaction from Left → Right. Given that many Hg(II) derivatives are insoluble then this clearly restricts the range of Hg(I) compounds.

### Minamata Disease

There have been several serious outbreaks of mercury poisoning. The most famous was between 1953 and 1965 at Minamata Bay in Japan when 46 people died and 120 suffered severe symptoms. As of March 2001, 2,265 victims had been officially recognised (1,784 of whom had died) and over 10,000 had received financial compensation from Chisso. By 2004, Chisso Corporation had paid $86 million in compensation, and in the same year was ordered to clean up its contamination. On March 29th, 2010, a settlement was reached to compensate as-yet uncertified victims. The disease was first noticed in cats (who were seen throwing themselves into the sea) and was quickly traced to mercury poisoning acquired as a result of eating contaminated fish (5-10 ppm Hg). The investigations that followed showed that the fish had acquired the high mercury due to the dumping of inorganic mercury salts and methylmercury from the Chisso Co. plastics factory upstream.

Analysis of fish exhibits from museums, some over 90 years old, has shown that mercury levels for ocean fish are similar but that river fish levels have risen as a result of man-made contamination. The forms of mercury occurring in the environment are Hg\(^{2+} \) and methylmercury, either MeHg\(^+ \) or Me\(_2\)Hg. Interconversion can be affected by microorganisms.

Aerobes can solubilise Hg\(^{2+} \) from cinnabar (\( K_{\text{sp}} \sim 10^{-53} \)) which in sediments was considered safe since the solubility product was so small. The conversion of \( S^{2-} \rightarrow SO_3^{2-} \rightarrow SO_4^{2-} \) allows the insoluble sulfide to breakdown and in the process other Hg(II) salts are formed or the mercury may get reduced to Hg(0) enzymatically.

\[
\text{Hg}^{2+} + \text{NADH} + \text{H}^+ \rightarrow \text{Hg}^0 + \text{NAD}^+ + 2 \text{H}^+,
\]

where NADH = reduced form of nicotinamideadeninedinucleotide

This conversion can be considered as a detoxification process since Hg\(^0 \) is more easily eliminated.

In the environment, sulfate-reducing bacteria take up mercury in its inorganic form and through metabolic processes convert it to methylmercury. Sulfate-reducing bacteria are found in anaerobic conditions, typical of the well-burried muddy sediments of rivers, lakes, and oceans where methylmercury concentrations tend to be highest. Sulfate-reducing bacteria use sulfur rather than oxygen as their cellular energy-driving system. One hypothesis is that the uptake of inorganic mercury by sulfate-reducing bacteria occurs via passive diffusion of the dissolved complex HgS. Once the bacterium has taken up this complex, it utilizes detoxification enzymes to strip the sulfur group from the complex and replaces it with a methyl group:

\[
\text{HgS} \rightarrow \text{CH}_3\text{Hg(II)}X + \text{H}_2\text{S}
\]

Upon methylation, the sulfate-reducing bacteria transport the new mercury complex back to the aquatic environment, where it is taken up by other microorganisms. Bacteria eliminate Hg by methylating it first to MeHg\(^+ \) and Me\(_2\)Hg. The
detoxification process for them is the reverse for us unfortunately! The conversion probably involves vitamin B12 a methyl-cobalt organometallic compound so this is another example of synthesis involving transmetallation.

The major source of methylmercury exposure in humans is consumption of fish, marine mammals, and crustaceans. Once inside the human body, roughly 95% of the fish-derived methylmercury is absorbed from the gastrointestinal tract and distributed throughout the body. Uptake and accumulation of methylmercury is rapid due to the formation of methylmercury-cysteine complexes. Methylmercury is believed to cause toxicity by binding the sulfhydryl groups at the active centers of critical enzymes and structural proteins. Binding of methylmercury to these moieties constitutively alters the structure of the protein, inactivating or significantly lowering its functional capabilities.

Once the Me₂Hg is formed it is volatile and when released into the atmosphere it is readily photolysed by UV light

\[ \text{Me}_2\text{Hg} \rightarrow \text{Hg}^0 + 2 \text{CH}_3{}^\circ \rightarrow \text{CH}_4 \text{ or C}_2\text{H}_6 \]

Other microorganisms can convert \( \text{MeHg}^+ \) to \( \text{Hg}^0 + \text{CH}_4 \) that is make the mercury considerably less toxic to humans.

The Mercury Cycle

Summary

Organic mercury tends to increase up the food chain, particularly in lakes. The mud at the bottom of a lake may have 100 or 1000 times the amount of mercury than is in the water. Bacteria, worms and insects in the mud extract and concentrate the organic mercury. Small fish that eat them further concentrate the mercury in their bodies. This concentration process, known as "bioaccumulation", continues as larger fish eat smaller fish until the top predator fish in the lake may have
methylmercury levels in their tissues that are up to 1,000,000 times the level in the water in which they live. We then eat the fish....

To consume a human being would be extremely unhealthy for any animal. Humans carry the highest concentration of toxic chemicals of all creatures on the planet. Their livers, hearts, kidneys and brains are so heavily contaminated with hundreds of different synthetic chemicals that if humans were slaughtered as a meat source, they’d never pass USDA food safety standards.

from Hg in Humans

Properties of Me₂Hg

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₂H₆Hg</td>
</tr>
<tr>
<td>Molar mass</td>
<td>230.66 g mol⁻¹</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless liquid</td>
</tr>
<tr>
<td>Density</td>
<td>2.96 g/mL</td>
</tr>
</tbody>
</table>
Melting point | -43 °C
Boiling point | 87-97 °C
Solubility in water | Insoluble

Laboratory Preparation:
Hg + 2 Na + 2 CH$_3$I → (CH$_3$)$_2$Hg + 2 NaI

$^1$H NMR of dimethylmercury showing $^{199}$Hg coupling ($J \sim 100.9$ Hz)
$^{199}$Hg has a nuclear spin of $\frac{1}{2}$ and natural abundance of 16.87%. Can you explain the observed splitting pattern?

Methylmercury
Dimethylmercury
Prof Wetterhahn -mercury

Tetraethyllead

Like mercury, lead is primarily obtained from its sulfide ore, in this case Galena, PbS, yet once again there are quite a number of other minerals containing lead. In terms of natural abundance it exists at about 14 ppm in the Earth's crust (37th compared to O), however it has become well known due to its ease of extraction and the number of uses with technical importance.
Lead was probably discovered around 6500 BC in Turkey and by 300 BC the Romans had lead smelters in operation. The toxicity of lead was recorded by the Greeks as early as 100BC. A report from 2BC noted that: "the drinking of lead causes oppression to the stomach, belly and intestines with wringing pains; it suppresses the urine, while the body swells and acquires and unsightly leaden hue".

The possible hazards associated with the use of lead piping in water systems was recognised as long ago as the first century BC and it has even been suggested that the "decline of the Roman Empire" might have been ascribed to the use of lead acetate as an additive to sweeten wine. It is somewhat surprising therefore that the first legislation controlling the industrial hazards of lead industries was not introduced until 1864.

Note that Dr. Wilton Turner (born in Clarendon, Jamaica in the early 1800's) wrote on the inappropriate use of lead in sugar and rum production while running a rum distillery in Guyana. One advocate said he had fed lead to dogs and guinea pigs for several weeks and seen no adverse affects in fact the guinea pigs were stolen which he thought was because they looked so fat and healthy!

An examination (in the early 1970's) of the annual snow strata in Northern Greenland and Poland revealed most elegantly that levels in air-borne lead had increased significantly since the Industrial Revolution and very sharply since 1940. Considering that 40-50% can be absorbed by inhalation compared to only 5-10% through ingestion this was cause for concern.
Leaded gasoline was an economic success from 1926 until 1976, and in fact, its discovery by Thomas Midgley at Charles Kettering's General Motors laboratory was among the most celebrated achievements of automotive engineering. It was often portrayed as the result of genius, luck and a great deal of hard work. It is now considered to be a catastrophic failure and is banned for environmental and public health reasons. (There are still a few countries selling petrol with lead additives.) Even more surprising is that the use of ethanol in fuel was already well established by the time tetraethyllead was introduced as an additive.

Tetraethyllead was supplied for mixing with raw gasoline in the form of "ethyl fluid", which was $\text{Et}_4\text{Pb}$ blended together with the lead scavengers 1,2-dibromoethane and 1,2-dichloroethane. "Ethyl fluid" also contained a reddish dye to distinguish treated from untreated gasoline and discourage the use of leaded gasoline for other purposes such as cleaning.

Ethyl fluid was added to gasoline in the ratio of 1:1260, usually at the refinery. The purpose was to increase the fuel's octane rating. A high enough octane rating is required to prevent premature detonations known as engine knocking ("knock" or "ping"). Antiknock agents allow the use of higher compression ratios for greater efficiency and peak power. The formulation of "ethyl fluid" was:

- Tetraethyllead 61.45%
- 1,2-Dibromoethane 17.85%
- 1,2-Dichloroethane 18.80%
- Inert materials and dye 1.90%

### Effect on Health

Humans have been mining and using this heavy metal for thousands of years, poisoning themselves in the process. Although lead poisoning is one of the oldest known work and environmental hazards, the modern understanding of the small amount of lead necessary to cause harm did not come about until the latter half of the 20th century. No safe threshold for lead exposure has been discovered, that is, there is no known amount of lead that is too small to cause the body harm.

Lead pollution from engine exhaust is dispersed into the air and into the vicinity of roads and easily inhaled. Lead is a toxic metal that accumulates and has subtle and insidious neurotoxic effects especially at low exposure levels, such as...
low IQ and antisocial behavior. It has particularly harmful effects on children. These concerns eventually led to the ban on Et₄PB in automobile gasoline in many countries. For the entire U.S. population, during and after the Et₄PB phaseout, the mean blood lead level dropped from 13 µg/dL in 1976 to only 3 µg/dL in 1991. The U.S. Centers for Disease Control considered blood lead levels "elevated" when they were above 10 µg/dL. Lead exposure affects the intelligence quotient (IQ) such that a blood lead level of 30 µg/dL is associated with a 6.9-point reduction of IQ, with most reduction (3.9 points) occurring below 10 µg/dL.

Also in the U.S., a statistically significant correlation has been found between the use of Et₄PB and violent crime: taking into account a 22-year time lag, the violent crime curve virtually tracks the lead exposure curve. After the ban on Et₄PB, blood lead levels in U.S. children dramatically decreased.

Even though leaded gasoline is largely gone in North America, it has left high concentrations of lead in the soil adjacent to all roads that were constructed prior to its phaseout. Children are particularly at risk if they consume this, as in cases of pica.

Note as well the work done in 1995 by ICENS on the problem of the old disused lead mine and tailings that affected school children in Kintyre. Over 40 cases were detected with unacceptable levels. ICENS at that time cleaned the community and sought to educate residents about the dangers. A continuation of the research done in Kintyre was to test 628 children at 17 basic schools across the island. Children at a number of basic schools in Kingston and St Catherine were discovered with blood lead levels as low as 45 µg/dL and as high as 60. In two of the cases, children had lead levels of 130 and 202. At this level, they would likely die from the poisoning if untreated.

**Properties of Et₄Pb**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₈H₂₀Pb</td>
</tr>
<tr>
<td>Molar mass</td>
<td>323.44 g mol⁻¹</td>
</tr>
<tr>
<td>Appearance</td>
<td>Colourless, viscous liquid</td>
</tr>
<tr>
<td>Density</td>
<td>1.653 g/mL (20 °C)</td>
</tr>
<tr>
<td>Melting point</td>
<td>-136 °C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>84-85 °C/15 mm Hg</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

**Laboratory Preparation:**
The industrial preparation of tetraethyllead was from the reaction below:

\[ 4 \text{NaPb} + 4 \text{EtCl} \rightarrow \text{Et}_4\text{Pb} + 3 \text{Pb} + 4 \text{NaCl} \]

or by electrolysis of NaAlEt\textsubscript{4} or EtMgCl using a Pb anode.

Laboratory syntheses of R\textsubscript{4}Pb compounds in general include the use of Grignard reagents or organolithium compounds.

\[ 2 \text{PbCl}_2 + 4 \text{RLi} \rightarrow \text{R}_4\text{Pb} + 4\text{LiCl} + \text{Pb} \]

References


3. DOI: 10.1021/om0101947
Contributors

- Template:ContribLancashire
- http://nptel.ac.in/courses/104101006/14