01 Apr 2005

Synthesis and characterization of Mercury vapor Coordination Species Using 1,3-Benzenedioethanethiolate (BDET)

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Synthesis and characterization of Mercury vapor Coordination Species Using 1,3-Benzenedioethanethiolate (BDET)

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Submitted April 1, 2005

Abstract

Mercury is a major pollutant in the air today. Some possible chelators that have been used are British anti-Lewisite (BAL) 2,3-dimercaptopropanol, dimercaptosuccinic acid (DMSA), dimercaptopropanesulfonic acid (DMPS), and 1,3-benzenediamidoethanethiolate (BDET). All contain two thiol groups, which 'capture' the heavy mercury element. Due to their structure, they all differ in how well they bind to the mercury atom. BDET is the most recent and efficient chelate used. Statistics show that coal-fired power plants are the nation's largest mercury polluter. Steps have been taken to lower the emission of this toxic metal by the Clean Air Act. However, recently The Bush Administration's Air Pollution Plan undermines the act. It delays the expectations and plans of the Clean Air Act by 10 years [1].

Introduction

Mercury has been a well-known hazard ever since the mad hatter cases in 1950 [2]. The heavy metal (also known as 'quick silver') affects the brain and nervous system and could sometimes lead to death. Much of the mercury that the average person has in his/her body is through the consumption of foods. The most common food that is contaminated with mercury is fish. Mercury has been a serious problem for years, but lately the Clean Air Act has been trying to control mercury pollution. The existing Clean Air Act states that mercury pollution will be down to 5 tons per year by 2008, from the current pollution of 48 tons per year [3]. Recently President Bush set forth a plan that will weaken the Clean Air Act.

Since most mercury pollution comes from coal-fired power plants, many businesses have been trying to reduce their production of mercury before the end of the decade. The main goal of this research project was to try to find a faster, more efficient, easier way to detect the amount of mercury that is being burned off in coal. One method that was looked at was to take a common chelator, specific to mercury, and polymerize it so it works similar to pH paper. Although the interaction would be would be vapor-solid state rather then

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liquid-solid state interaction. The following is a discussion about mercury pollution today, different chelators of mercury, and a possible chelator that could be used.

Regulation of Mercury

The nations largest mercury polluters are coal-fired power plants. They produce about one third of the mercury in the air [3]. The mercury vapors contaminate lakes, rivers, soil, and streams, thus producing serious health risks. At this time the Environmental Protection Agency (EPA) is required by law to issue "maximum achievable control technology" (MACT) standards for coal-fired power plants by the end of 2007 [3]. Currently the Clean Air Act (CAA) has a plan to reduce mercury pollution. If MACT is installed into most coal-fired power plants then mercury should be reduced from 48 tons per year to 5 tons a year by 2008. However, President Bush has just recently brought a plan that would weaken the progress of the CAA by 10 years! President Bush's plan would allow for 26 tons per year by 2010 and 15 tons per year by 2018 [1].

Another major difference would be that the CAA would require mercury reductions in *each* power plant, where Bush's plan would allow unrestricted emissions trading. Meaning that businesses would be allowed to buy their way out of the plan. The business would simply buy mercury emission 'credit' from other businesses instead of reducing the amount of mercury being emitted. This would lead to very toxic 'hotspots' and worsen the problems in that specific area.

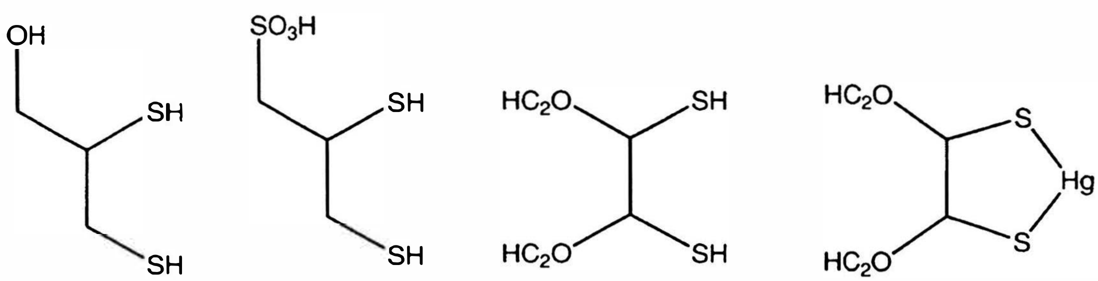
Mercury Removal

Both plans require that mercury be controlled. One way that mercury is being removed from the fumes caused by coal burning uses a regenerable sorbent. It allows mercury to be recovered and recycled by triple distillation. The sorbent was developed by ADA Technologies and the entire process is called "Mercu-Re process" [4]. The process allows noble metals to repeatedly sorb and desorb mercury compounds at flue-gas conditions. This system has mercury removal effectiveness above 95%, regardless of the chemical form of the mercury [4]. The types of mercury forms are methylmercury ($HgCH_3$), mercuric chloride ($HgCl_2$), mercuric oxide (HgO), and elemental mercury (Hg). Methylmercury is the form that is very toxic and contaminates most fish. Although this technique is very effective, it is costly and takes up a great amount of space. ADA Technologies expect the cost of their system to be $866,000 per year for a 250 MW plant [4].

Chelators

A chelator is a molecule that binds to a metal ion by at least two functional groups to form a stable complex. This stable complex is known as a chelate. The first chelator, British anti-Lewisite (BAL, Figure 1A), was used for the removal of the arsenical war gas Lewisite. Due to its low solubility and horrible smell dimercaptopropanesulfonic (DMPS, Figure 1B) was produced. DMPS had better solubility and was nearly odorless. Later dimercaptosuccionic acid (DMSA, Figure 1C) was introduced with approximately the same properties of DMPS [5].

DMPS and DMSA were originally used for chelation therapy. Chelation Therapy is the removal of mercury from the body. They work fairly well, but are unable to remove mercury from the brain due to lack of access. Another problem with both complexes is that they tend to form different species other then DMSA-Hg complex (Figure 1D) and DMPS-Hg. Possible species may include $Hg_2(DMSA)_2$, $Hg_3(DMSA)_3$, or the similar species with DMPS [5]. These species would bear high negative charges and would not be very stable. Also for a drug to be effective for chelation therapy, it must bind effectively all by itself (without any additional molecular entity) [5]. Studies have shown that these chelators are somewhat effective, but not the best option.



A B C D

Figure 1
(A) BAL, (B) DMPS, (C) DMSA, (D) DMSA-Hg complex.

A recent complex has been developed that seems to 'trap' the mercury element more effectively. The complex is called 1,3-benzenediamidoethanethiolate (BDET, Figure 2 & Figure 3). Studies have shown that it has a high affinity for soft heavy metals such as: Cu^{+2}, Cd^{+2}, Mn^{+2}, Pb^{+2}, Hg^{+2}, and Zn^{+2}. When it binds to one of the metals the species formed precipitates out. The complex is stable under low and high pH and strongly oxidizing conditions [6].

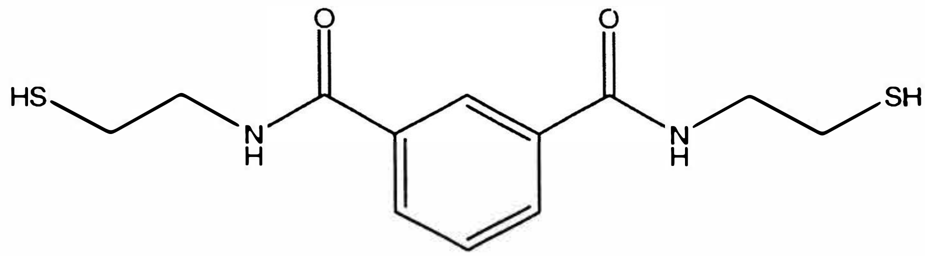


Figure 2
The stick model of BDET

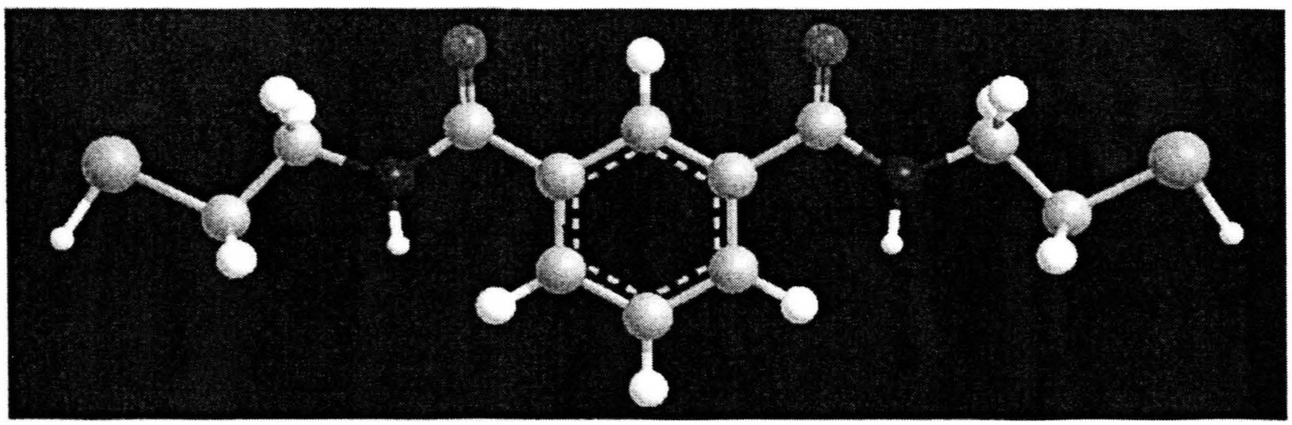


Figure 3
A ball and stick model of BDET complex. Carbon = light grey, Hydrogen = white; Oxygen = red; Nitrogen = blue; sulfur = yellow

When the mercury element binds to BDET, it will most likely form the structure shown in Figure 4 & Figure 5. The benzene ring will arrange itself so that the complex formed will be stable. The reaction that takes place has the following equation [7]:

$$C_{12}H_{16}N_2O_2S_2 + M^{2+} + 2H_2O \rightarrow C_{12}H_{14}N_2O_2S_2M\downarrow + 2H_3O^+$$

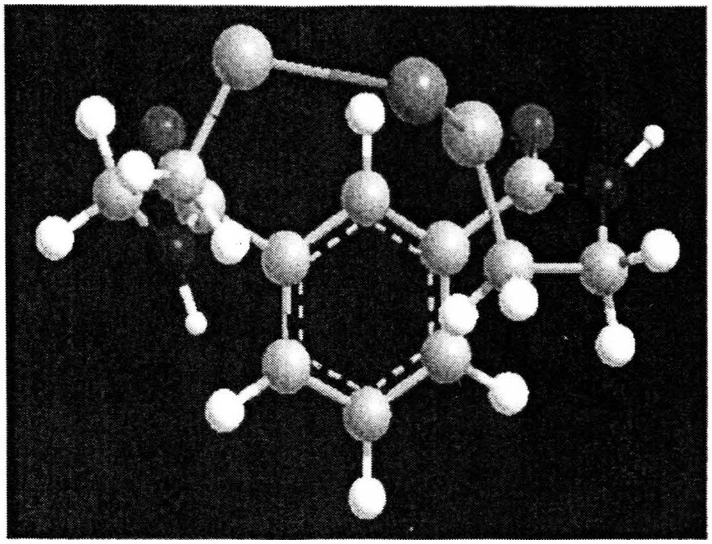


Figure 4
A side view of BDET- Hg complex. The color scheme for the atoms is the same as what was used in Figure 3 with Mercury = dark grey.

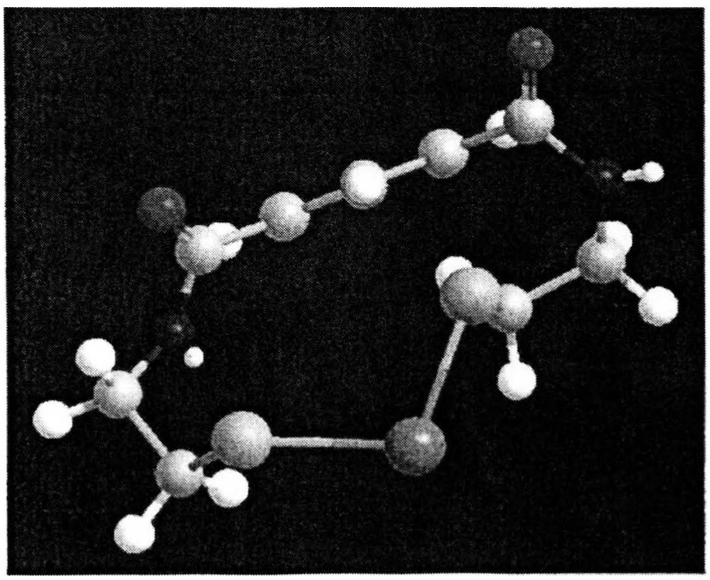


Figure 5
Top view of BDET-Hg complex. Showing the orientation of the benzene ring.

Allowing BDET to bind to a polymer (Figure 6) and still be effective is the next step in the research of this species. Still to be investigated is the mercury vapor interaction with the solid form of BDET. A possible problem would be whether or not the BDET being bound to a polymer will affect it from moving its side 'arms' to capture mercury.

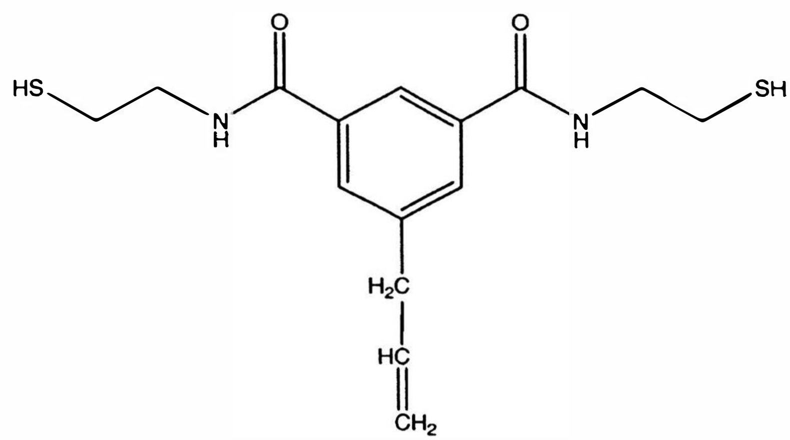


Figure 6

Conclusion

Even though mercury has been a well-known poison to humans and the environment, the control and pollution of the harmful element has just begun. Many steps have been taken to help limit and lower the emissions of mercury from coal-fired power plants, but President Bush's plan seems to dilute the CAA's plans for the future. In either case, steps have been taken to produce the best way of detecting and removing mercury from the vapors of the burning coal. However, since BDET is a fairly new compound, future studies are still to come to produce more information on the application and use of BDET.

Acknowledgement

The work and research was supported by Opportunities for Undergraduate Research Experiences (OURE) at the University of Missouri – Rolla. I would also like to thank Prof. Harvest Collier for his guidance and help throughout the year.

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