Report for 2004TN12B: Removal of Toxic Heavy Metals from Wastewater Effluents

- Articles in Refereed Scientific Journals:
    - Grant, G J, L L Hill, M L Helm, D G VanDerveer, 2005, Multinuclear NMR Studies on Homoleptic Thioether Complexes of Cadmium(II), J Chem Soc Dalton Trans, submitted.
    - Helm, M L, G P Helton, D G VanDerver, G J Grant, 2005, 199-Hg NMR Chemical Shifts in Thiacrown and Related Macrocyclic Complexes, Inorganic Chemistry, in press.
- Book Chapters:
    - Grant, G J, 2005, Mercury(II) Complexes with Thiacrown Ligands, invited chapter in Structure and Bonding, in preparation.

Report Follows

Problem and Research Objective:
The critical water issue addressed by our research project was water quality. The project dealt with research that can lead to enhanced methods for the treatment, removal, and detection of hazardous and toxic heavy metal contaminants in industrial and municipal wastewater. These heavy metal pollutants are problematic because their presence may not be obvious, and even when present at very low concentrations, they may have insidious effects. Industries present in the state of Tennessee such as mining and smelting can mobilize large quantities of trace metals. Besides industrial sources, solid waste disposal and landfills create another potential source of these heavy metals which can pollute groundwaters. For example, discarded household batteries, inks, paints and dyes, dental amalgams, and pigments can release heavy metals into water supplies. Thus, sewage sludge disposal and landfills can also result in an increase of trace metals in surface or groundwater, and special waste disposal in approved landfill sites has previously been employed for the handing of some toxic heavy metals in the state of Tennessee.

The specific goal of this research project was to examine correlations between X-ray crystal structures and NMR chemical shifts for complexes containing the divalent heavy metal ions Hg(II) and Cd(II). The research project can assist in the further advancement of chemosensors for heavy metal ions by providing key information regarding their solution structures. We are currently focusing on macrocyclic thioether complexes of heavy metal since nuclei like 199Hg and 113Cd are attractive and amenable for study by NMR yet surprisingly little data exist for them.

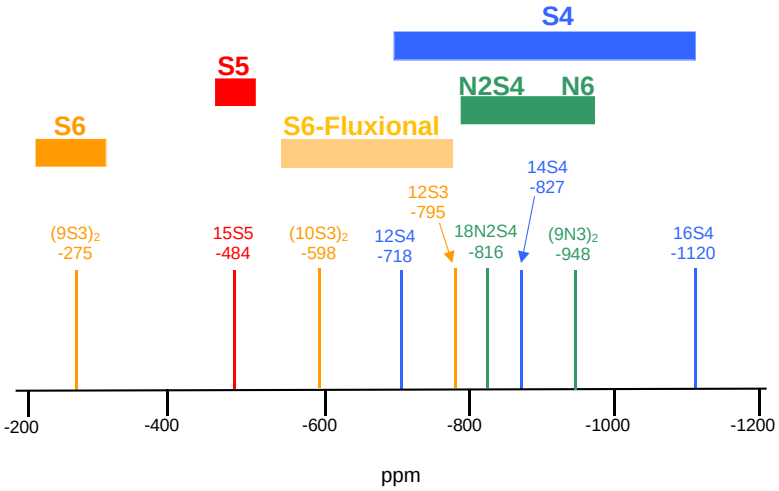
Objectives of Research:
The research objectives of this project were to:

(1) Synthesize novel complexes containing several polythioethers with heavy metal ions such as mercury and cadmium.
(2) To characterize and analyze these complexes using multinuclear nuclear magnetic resonance including 199Hg and 113Cd NMR
(3) To examine the NMR behavior and identify trends in data.

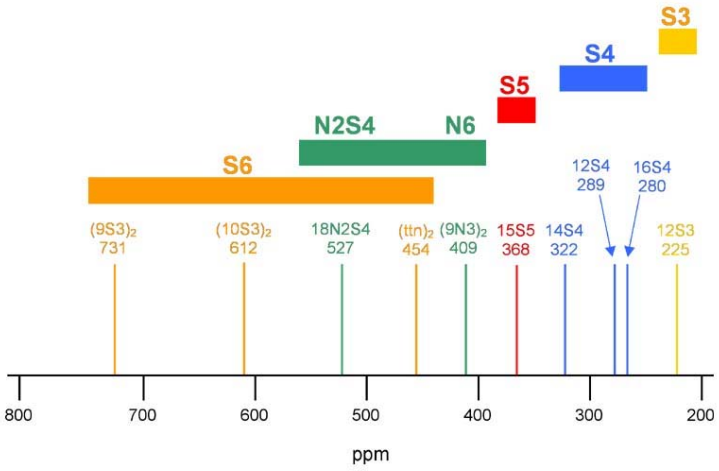
Research Results and Findings:
We have now prepared many complexes containing several polythioethers with two heavy metal ions, mercury, and cadmium. Additionally, these mercury and cadmium complexes have been characterized and analyzed using nuclear magnetic resonance spectroscopy. We wish to report our NMR results for a series of Hg(II) and Cd(II) complexes containing thiacrown ligands as well as some related azacrowns and mixed nitrogen-sulfur donor ligands.

We observe 113Cd NMR chemical shifts in the range of 730 to 225 ppm and 199Hg NMR chemical shifts in range of –275 to –1120 ppm for the series of macrocyclic complexes. Graphical summaries of our data with both nuclei appear on the following page.

199Hg NMR chemical shift data



$^{113}Cd\{^{1}H\}$ NMR Shifts of Various Thioether Complexes

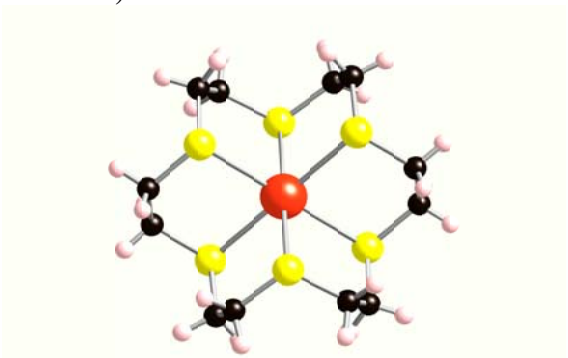


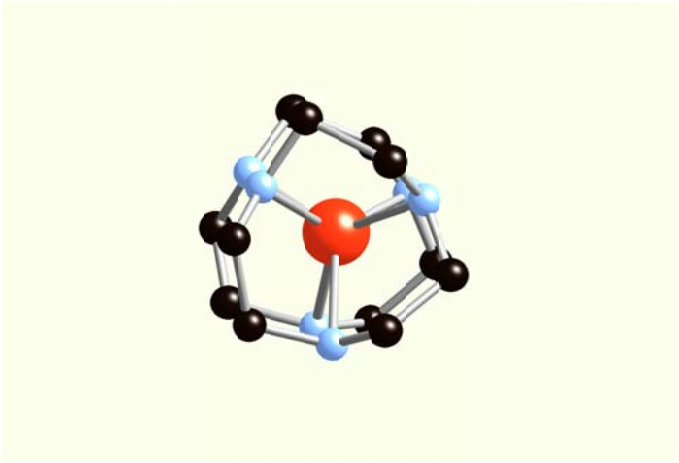
To summarize these data -- Upfield chemical shifts in the NMR spectra of either nucleus are seen whenever:

1. the number of thioether sulfur donors in the complex is decreased.
2. a thioether sulfur donor is replaced by a secondary nitrogen donor.
3. the size of the macrocycle ring increases without a change in the nature or number of the donor atoms.

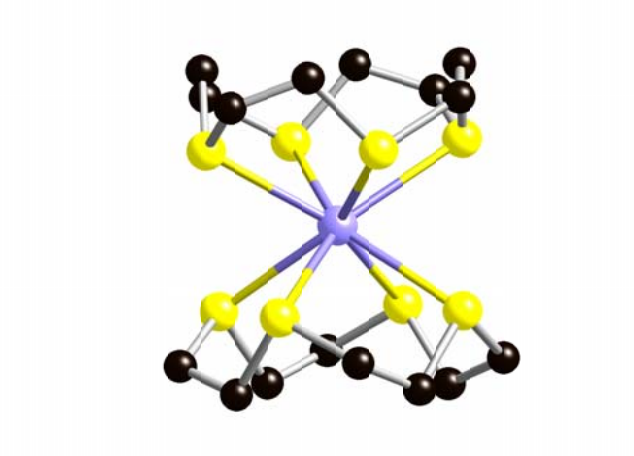
Thus, we have developed a novel means of clearly identifying the surrounding ligand environment for mercury or cadmium in solution.

We report the crystal structures of the mercury(II) complexes with the crown thioether 18S6 as well as the bis complex with azacrown 9N3. The two structures are shown below. An interesting structural result that we have obtained is complexes with six sulfur donors bonded to mercury(II) have an octahedral structure while complexes with six nitrogen donors have a trigonal prismatic structure as shown for the 9N3 complex (2nd structure) below.





We also report the crystal structure for the bis cadmium(II) complex with the tetrathiacrown 12S4. An unusual octakis(thioether) coordination of Cd(II) with a square anti-prismatic geometry is exhibited by [Cd(12S4)2](ClO4)2is shown.



Summary

We have established clear trends in how changes in the ligand environment around a mercury or cadmium center affect its NMR chemical shift. This information will be invaluable for the design of ligand systems which can selectively bind these heavy metals and in chemosensors that are used to detect them.

Presentations at Conferences and Universities Resulting from the Project.

This work has resulted in six presentations at conferences and Universities during the past twelve months. The presentations are listed below, and the name of the author is underlined. These all acknowledge the generous support of the Tennessee Water Resources Research Center. Presentation #1 was an invited paper in a special Symposium on Mercury Immobilization in Soil and Water that was part of a regional chemistry meeting in November of 2004. Paper #3 was presented at an international chemistry conference in Australia.

1. Gregory J. Grant, Monte L. Helm, Gregory P. Helton, Lensey L. Hill "Applications of 199Hg NMR Spectroscopy in Heavy Metal Complexes of Thiacrown Ligands" presented at the 56th Southeastern Regional Meeting of the American Chemical Society, Research Triangle, NC, November 10-13, 2004. Symposium on Mercury Immobilization in Soil and Water, Environmental Chemistry and Public Health Issues. Paper Number 742.

2. Maikel E. Botros, Gregory J. Grant, "Synthesis of the Mixed Donor Macrocycle, 9S2N, 7-aza-1,4-dithiacyclcononane" presented at the 56th Southeastern Regional Meeting of the American Chemical Society, Research Triangle, NC, November 10-13, 2004. Undergraduate Research Poster Session, Division of Chemical Education Paper Number 874.

3. Gregory J. Grant, Monte L. Helm, Gregory P. Helton, Lensey L. Hill; "199Hg and 113Cd NMR Analysis of Macrocyclic Thioether Complexes" presented at the 29th International Symposium on Macrocyclic Chemistry; Cairns, Queensland, Australia, July 4–8, 2004. Paper Number P18.

4. Gregory J. Grant; "Lords of the Thioether Rings: Mercury(II) and Platinum(II) Complexes of Thiacrown Ligands"; invited departmental seminar; presented to the Department of Chemistry, Clemson University Clemson, SC April 28, 2005.

5 Gregory J. Grant, Monte L. Helm, Gregory P. Helton, Lensey L. Hill; "199Hg and 113Cd NMR Analysis of Macrocyclic Thioether Complexes" presented at the 229th National Meeting of the American Chemical Society, San Diego, CA, March, 13-17, 2005. Division of Inorganic Chemistry, Paper Number 705.

6. Maikel E. Botros, Gregory J. Grant, "Synthesis of the Mixed Donor Macrocycle, 9S2N, 7-aza-1,4-dithiacyclcononane" presented at the 229th National Meeting of the American Chemical Society, San Diego, CA, March 13-17, 2005. Undergraduate Research Poster Session, Division of Chemical Education Paper Number 545.

Student Involvement in the Research:
Two UTC students were funded through the project, Greg Helton and Maikel Botros. Both presented their work at professional meetings and were included as co-authors on presentations made by Dr. Grant. Helton is a co-author on one paper (Paper #2) that has already been accepted for publication, and the two students will be co-authors on at least two additional papers. Both students are interested in medical school, and Greg Helton is currently applying to the University of Tennessee at Memphis medical school.