The Inert Pair Effect: Relative Stabilities of Tin(IV) and Pb(IV)

ABSTRACT
For p-block elements, two main oxidation states are available, one derived from the loss of the element's p electrons and the other derived from the loss of the s and p electrons. The former becomes more stable than the latter as the group is descended. This experiment uses a series of syntheses and qualitative redox tests to show that Sn(IV) is more stable than Sn(II) in aqueous environments, in contrast to Pb(IV), which is less stable than Pb(II).

Equipment
No special equipment required. Some tests should be done in a fumehood. Test tubes, spatulae, beakers, etc.

Safety Hazards
No particular hazards. Tin and lead compounds are toxic. Halogenated solvents are considered carcinogenic.

Year Level:	2nd year introductory inorganic
Student time required:	two 3-hour lab periods
Instructor time required:	~3 hours??
Technician notes?	Available upon request
Study question solutions?	Available upon request
Contact:	Craig MacKinnon (craig.mackinnon@lakeheadu.ca)

Lakehead
UNIVERSITY

Chemistry 2351: Inorganic Chemistry I
Laboratory Manual

Instructor: C. D. MacKinnon
Department of Chemistry
Faculty of Science and Environmental Studies

Experiment Two:

The Inert Pair Effect: Relative Stabilities of Tin(IV) and Lead(IV)

Purpose of the Experiment

In this experiment, the student will examine the stability of +4 oxidation states of tin and lead. The redox, acid/base and solubility chemistry of the +2 and +4 oxidation states of these elements will also be examined.

Introduction

The elements of Group 14 are characterized by an s^2p^2 electronic configuration. Thus, the members of this group often use their four valence electrons to form four σ-bonds. The heavier members of the Group (heavier than carbon) are also capable of achieving higher coordination numbers (*i.e.* six-coordinate) by using their *d*-orbitals. In general, the elements of this Group are often described by a +4 oxidation state when bound to atoms of greater electronegativity (*e.g.* halides). However, as one proceeds down the group, the stability of the +4 oxidation state decreases and, in fact, there is a greater tendency to form compounds possessing a +2 oxidation state. Thus, the inner shell s^2 electrons of the heavier elements (*e.g.* lead) are often not used in bonding; that is to say, they act as an *inert pair* of electrons. In general this phenomenon is referred to as the *inert pair effect* and it is also observed in other heavier main group nuclei such as thallium (+1 *vs.* +3), lead (+2 *vs.* +4), and bismuth (+3 *vs.* +5), where the lower charged ions are more stable than the more highly charged ions.

Lead(IV) is generally only stable when bonded to highly electronegative ligands (*e.g.* O^{2-}), and Pb(IV), is easily reduced to Pb(II). For tin, the +2 and +4 oxidation states are similar in stability. In this experiment, the student will have the opportunity to prepare Sn(IV) and Pb(IV) complexes in the form of $(NH_4)_2MCl_6$ (M = Sn or Pb), and observe firsthand the relative stabilities of both. A number of qualitative tests will be conducted in order to compare the stability of the +2 and +4 oxidation states of tin and lead, as well as examine some of the redox chemistry of each element.

Experimental Procedure

Special Notes and Safety Precautions

A number of reagents are used in each preparation which require special attention. $SnCl_4$ fumes in open air; the fumes are very corrosive and must never be inhaled. All manipulations of this reagent must be performed in the fumehood, and exposure to the open air must be minimized. Be sure to promptly cap the bottle when not in use. Like all lead compounds, the lead reagent used in this experiment, $Pb(NO_3)_2$, and its products are all poisons. Any skin contact with these materials must be avoided. Gloves must be worn when manipulating these materials. Flush all areas with copious amounts of water where contact has been made. In several preparations acids and bases are used. Care must be exercised when using these solutions and all exposed areas must immediately be flushed with water.

Synthesis of Ammonium Hexachlorostannate(IV), $(NH_4)_2SnCl_6$

In the fumehood, add a volume of saturated NH_4Cl solution (5 mL) to a clean, dry 10 mL beaker, and then *slowly and cautiously* add 1.8 mL of $SnCl_4$ to the solution, with stirring (glass rod). Once the mixture stops fuming, cool the mixture in ice until crystals of $(NH_4)_2SnCl_6$ begin to deposit. Filter the crystals (Büchner) and allow them to dry in the air (do not wash the crystals with water as they are quite soluble; if necessary, use ice-cold water). Record the yield and set the product aside for the qualitative tests to follow.

Synthesis of Ammonium Hexachloroplumbate(IV), $(NH_4)_2PbCl_6$

(a) Synthesis of PbO_2 from $Pb(NO_3)_2$. Prior to preparing the title complex, PbO_2 must first be prepared. In a 250 mL beaker, add $Pb(NO_3)_2$ (about 4 g, **accurately weighed**) and dissolve it in water (25 mL). Next, prepare a solution of NaOH (*aq*) by dissolving NaOH (10 g) in a separate 150 mL beaker with water (50 mL). Add the solution of NaOH to the 250 mL beaker with stirring and *carefully* boil the mixture for 5-10 minutes on a hotplate. Next, while continuously stirring the hot mixture, slowly add a solution of NaOCl (20 mL of a 5% solution); *keep the solution hot and be sure to maintain constant stirring during the addition of the NaOCl.* The deep, dark brown-black precipitate that forms is PbO_2 (this should form after 5-10 minutes). Filter the solution hot (Buchner), wash the product with water (3 × 10 mL), followed by dilute HNO_3 (3 × 5 mL of a 2 M solution), and then again with water (10 mL). The PbO_2 does not have to be dry for the next stage of the reaction. Also, it may be stored in the locker until needed. In either case, set aside a small portion (about 0.5 g is enough) of the PbO_2 for use in the qualitative tests.

(b) Synthesis of $(NH_4)_2PbCl_6$ from PbO_2. It is imperative that the following reactions be performed in *ice-cold solutions*. In a 50 mL beaker add a volume of saturated NH_4Cl solution (10 mL), and in a 10 mL beaker add concentrated (*care!*) HCl (5 mL). Cool both solutions thoroughly in ice. With the beaker containing the HCl still in the ice bath, slowly add PbO_2 (prepared above), with constant stirring (glass rod); a yellow solution should be obtained. In some cases, a small amount of white precipitate will appear at this stage; this does not influence the outcome of the reaction, however note its appearance and keep it in mind when conducting the tests that follow. In the event that some white precipitate does appear after adding all of the PbO_2, leave the yellow solution in the ice bath for a few minutes so as to allow it to settle. Next, quickly but carefully decant the yellow solution into the ice-cold NH_4Cl solution (still in the ice bath) with stirring, making sure to leave behind any white solid that may have previously appeared. Allow the mixture to sit in the ice bath for several minutes in order to complete the precipitation, and then filter the $(NH_4)_2PbCl_6$ product (Buchner) from the mixture. Do not wash the product with water as it is very soluble in this solvent. Allow the product to air dry (they may be stored in the locker until the next laboratory session) and record the yield.

Qualitative Analysis of Tin and Lead

Perform the following qualitative tests and record ALL observations. Be prepared to observe NO reaction in some cases!

(1) Place a portion of each ammonium salt in separate test tubes and add a little water. Carefully heat both solutions for several minutes in a hot water bath and observe; allowing each tube to sit in an ice bath after heating will assist in making any observations.

(2) Place a portion of each ammonium salt in separate test tubes and add a little water. To each tube add $CHCl_3$ (1 mL) followed by 5-10 drops of KI solution acidified with a few drops of dilute (2 *M*) H_2SO_4. Stopper and shake both tubes, and observe.

(3) Make solutions of Sn(II) and Pb(II) as follows:
- dissolve 2 g $SnCl_2 \bullet 2H_2O$ in HCl (10 mL of a 0.1 M solution); centrifuge and use the solution
- dissolve 2 g $Pb(NO_3)_2$ in water (10 mL)

perform the following tests:

(i) To small portions (about 1 mL) of each in individual test tubes, add a few drops of $KMnO_4$ solution that has been acidified with a few drops of dilute (2 M) H_2SO_4 and observe.

(ii) To a small portion of the Pb(II) solution in a test tube, add a couple of drops of concentrated (*care!*) HCl and observe. Similarly but with a fresh sample, add a few drops of KI solution and observe.

(iii) To small portions of each solution in individual test tubes, add a few drops of Na_2SO_4 solution and observe.

(iv) To a small portion of the Sn(II) solution in a test tube, slowly add NaOH (2 M) dropwise with mixing until no further changes are observed. Observe the change(s).

(4) In two separate test tubes place a small volume (about 1 mL) of KI solution acidified with a few drops of dilute (2 M) H_2SO_4, followed by $CHCl_3$ (about 1 mL). Next, add a small amount of PbO_2 to one tube and SnO_2 to the other, stopper each tube and shake. Note any results.

(5) In two separate test tubes, dissolve a few *crystals* (this is all that is required; any more than this and the reaction may be difficult to observe) of $MnSO_4$ in dilute (2 M) HNO_3 (a few mL is all that is required). To one tube add some solid PbO_2, the other SnO_2. Carefully boil each mixture and observe the results.

Final Report

Complete the report sheet (located at the end of this manual). Remember that a separate sheet containing a table of your observations must be attached to the report sheet.

References/Bibliography

General information: Miessler and Tarr, Inorganic Chemistry, 3rd Edition (2351 text)
Zumdahl and Zumdahl, Chemistry, 8th Edition (1110/1130 text)

redox chemistry: Wulfsberg, Inorganic Chemistry (library course reserve)

synthetic reference: Brauer, Handbook of Preparative Inorganic Chemistry - Vol. 1, 2nd edition (library course reserve)

CHEMISTRY 2351 REPORT SHEET
Experiment Two:
The Inert Pair Effect and the Relative Stabilities of Tin(IV) and Lead(IV)

NAME:_____

DATE: _____

Synthesis of ammonium hexachlorostannate (IV)

Balanced reaction:

Limiting reagent: _____ Mass of limiting reagent: _____

Yield _____ % Yield _____ Colour: _____

Synthesis of ammonium hexachlorostannate (IV)

Balanced reaction:

Limiting reagent: _____ Mass of limiting reagent: _____

Yield _____ % Yield _____ Colour: _____

Write the equation(s) that describe the synthesis of $(NH_4)_2PbCl_6$ starting from Pb(II) [*i.e.* $Pb(NO_3)_2$]. Hint: There is a redox reaction in the first step, where the bleach (ClO^-) is the oxidising agent.

Experiment 2 Report Sheet **NAME:_____**

In tests (2) and (4), what purpose does the $CHCl_3$ serve?

While PbO_2 and $PbCl_4$ exist, $PbBr_4$ and PbI_4 do not. Why?

On a separate page, make a table including all qualitative observations (*i.e.* colours of the products and solutions, gas evolution, no reaction, etc.). For each of the tests (1) to (5), write the balanced ionic equations for those reactions that were observed to occur. Include potentials where possible.