Experiment 18 NMR lead 207.

SYNOPSIS

The natural abundance of 207-Pb is determined by proton NMR from a lead-EDTA chelate. The structure of binding of EDTA-Pb in solution is also investigated.

READINGS *Review all preceding labs on EDTA and Lead. Review labs on pH, Read section on EDTA and again EDTA and NMR (pages 325-329 in Critical Reviews), also read section in IR and EDTA: (pages319-325).*

Caution

This lab is extremely sensitive to the mole ratio of EDTA to Pb and to the pH. The binding of lead to EDTA changes with pH, which changes the linewidths so that resolution can be lost. Furthermore the ^{207}Pb coupling through the nitrogen depends on the half life of that bond which is also dependent upon the mole ratio and pH.

INSTRUMENT

pH meter
NMR (Varian EM 360A 60 MHz magnet coupled to an Elbit ATI series 2000 FT console)

CHEMICALS

TMS as a reference
D_2O
$Pb(NO_3)_2$
Na_2EDTA
Sodium bicarbonate
Sodium carbonate

Buffer Preparation (pH 9.2)

0.2 M Na_2CO_3 = 0.0212 g of anhydrous Na_2CO_3 in 1 mL of D_2O
0.2 M $NaHCO_3$ = 0.0168 g of anhydrous $NaHCO_3$ in 1 mL of D_2O

Combine 0.46 ml of 0.2 M soidum bicarbonate with 0.04 mL of 0.2 M sodium carbonate and dilute it with 0.5 ml of D_2O.

Note: A better NMR spectrum resolution can be obtained by adjusting the sample pH with dilute NaOD instead of using the buffer. However, the final volume (if needed) would have to be measured after the pH is adjusted. Also a small pH electrode would be needed.

Sample Preparation

Dry the powdered lead nitrate two hours at about 130 C to remove water.
Dry the Na_2EDTA-H_2O 4 days at 100°C to remove water. The molecular weight of the dried EDTA is 336.2 g/mole.

Preparation of a 1:1 mole ratio EDTA/Pb.

0.0250 g Na_2EDTA * 1 mole Na_2EDTA/336.2 g = $7.437x10^{-5}$mole Na_2EDTA
$7.437x10^{-5}$ mole Na_2EDTA * 1 mole $Pb(NO_3)_2$/1mole Na_2EDTA *####/1mole $Pb(NO_3)_2$
= 0.02463g $Pb(NO_3)_2$

1. Combining equal molar amounts of Na^2EDTA (0.0250 g) and $Pb(NO_3)_2$ (0.02463g) in a Wheaton 4 ml sample vial.
2. Add 0.8 mL of D_2O. A white precipitate will be formed. Add NaOD.
3. Sonicate (about 5 min.) at room temperature to speed up the EDTA/Pb complex formation.
4. As soon as there was no solid material left in the vial the sample was transferred to an NMR tube.
5. Perform all references against water.

Note to instructor: Samples of the pure EDTA at this buffer should be obtained also.
Students may wish to observe the change in the EDTA with pH by changing the bicarbonate buffer.
Students may wish to observe the change in the spectra with different mole ratios of lead to EDTA. The best experiment is to ***increase*** *the amount of* ***lead*** *present.*

METHOD

1. Obtain an NMR spectra for each of the solutions
2. On the spectra acquire the peak area separately for each of the doublet peaks and the central peak.

REPORT

1. Identify the major peaks in your NMR spectrum. (Recall that the peak heights correlate with the number of protons.)
2. Why don't the ethylenic protons shift to the same extent as the acetate protons?
3. Would you expect differences in this spectrum and that of Zn-EDTA? Do you think you could resolve the two species if they were present simulataneously in your sample?
4. Compute the % relative abundance of lead 207from the side bands. Does your value compare well with the published data?

5. Would you be able to tell the difference between a lead ore from two different mines with this method. (Calculate the std. deviation and compare it to the std. Deviation associated with variation in207-Pb.
6. Can you think of a use for this method with respect to the analytical issues faced in the lead-environmental controversy?
7. Why can't we perform the analysis in water?
8. Compute the % natural abundance of 207-Pb.
9. Measure and identify the chemical shift associated with the protons in EDTA in each of the 5 spectra.
10. Measure the spin-spin coupling constant, $J_{(Pb\text{-}H)}$, for the ^{207}Pb derived doublet.
11. Measure the peak width at half height for the doublet peaks associated with ^{207}Pb in each spectra.
12 From the peak width calculate the lifetime of the complex.
13. Plot the lifetime of the complex as a function of mole fraction of the complex.
14. What importance might the lifetime of the chelate-metal complex have on use of the chelate in lead poisoning therapy?
15. Are there any problems with disposal of hazardous materials?
16. How easy would it be to instruct a technician on this method?