

“A” students work
(without solutions manual)
~ 10 problems/night.

Dr. Alanah Fitch
Flanner Hall 402
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Office Hours Th&F 2-3:30 pm

Module #18:
Complex Ions:
Saving future
Mr. Litvinenkos

FITCH Rules

G1: Suzuki is Success
G2: Slow me down
G3: Scientific Knowledge is Referential
G4: Watch out for Red Herrings

G5: Chemists are Lazy

C1: It's all about charge $E_{el} = k \left(\frac{q_1 q_2}{r_1 + r_2} \right)$
C2: Everybody wants to “be like Mike”

C3: Size Matters

C4: Still Waters Run Deep Piranhas lurk

C5: Alpha Dogs eat first

What is an alpha dog?
 High charge, low volume

An Example of rate constants in the real world: context and calculations

Toxicology of Radioactive Exposure

$^{210}_{84} Po \rightarrow ^4_2 He + ^{206}_{92} Pb$

Alexander Litvinenko, former Russian KGB agent
poisoned with Polonium on Nov. 1, died Nov. 23, 2006

190 ng dose suspected

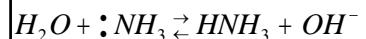
Could it be
Removed using
Complexation
reactions?

Review: Module 15: Kinetics and Biology

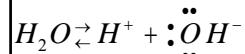
How and where Po might go depends upon its chemistry

1. Same family as O, S, and Se, Te
 $Po = [Xe]6s^2 4f^{14} 5d^{10} 6p^4$
2. But with a smaller ionization energy
 $M \rightarrow M^+ + e$
3. it does not form covalent bonds
E.N. = 2.0 for Po vs. 2.55 for C and 3.44 for O
4. Forms ionic, soluble compounds
 $PoCl_2, PoCl_4, PoBr_2, PoBr_4, PoI_2, PoI_4, PoO_2$

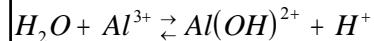
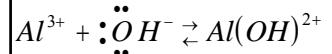
Review: Module 15: Kinetics and Biology elements/text/Po/energ.html



N is a Lewis:
Base (**Electron pair donor**)



O is a Lewis Base
(**Electron pair donor**)



Al³⁺ is a Lewis:
Acid (**Electron pair acceptor**)



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Types of Ligands

Ligand from Latin *ligare* “to bind”

“a molecule or anion with an unshared pair of electrons donating a lone pair to a metal cation to form a coordinate covalent bond”

Elements with unshared pairs of electrons capable of being ligands:
C, N, O, S, F, Cl, Br, I

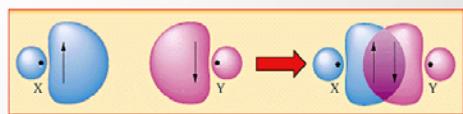
Molecules acting as ligands:
:NH₃; :OH₂

Ions acting as ligands:
Cl⁻, Br⁻, I⁻, [C≡N]⁻

<http://chem.chem.rochester.edu/~chemlab2/Lecture%203%202-12-07%20Fe-oxalate%20synthesis.pdf>

Covalent/Coordinate-Covalent Bonds

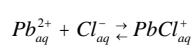
Normal covalent: metal ion X and ligand Y each contribute one e⁻



Coordinate-covalent: both e⁻ come from the ligand



Example 2: A complex formed from a ligand and a metal



$$K_{f1} \quad K_{f1} = \frac{[PbCl_{aq}^{+}]}{[Pb_{aq}^{2+}][Cl_{aq}^{-}]} \quad \boxed{[PbCl_{aq}^{+}] = K_{f1} [Pb_{aq}^{2+}][Cl_{aq}^{-}]}$$



$$K_{f2} \quad K_{f2} = \frac{[PbCl_{2,aq}^0]}{[PbCl_{aq}^{+}][Cl_{aq}^{-}]}; \quad \boxed{[PbCl_{2,aq}^0] = K_{f2} [PbCl_{aq}^{+}][Cl_{aq}^{-}]}$$

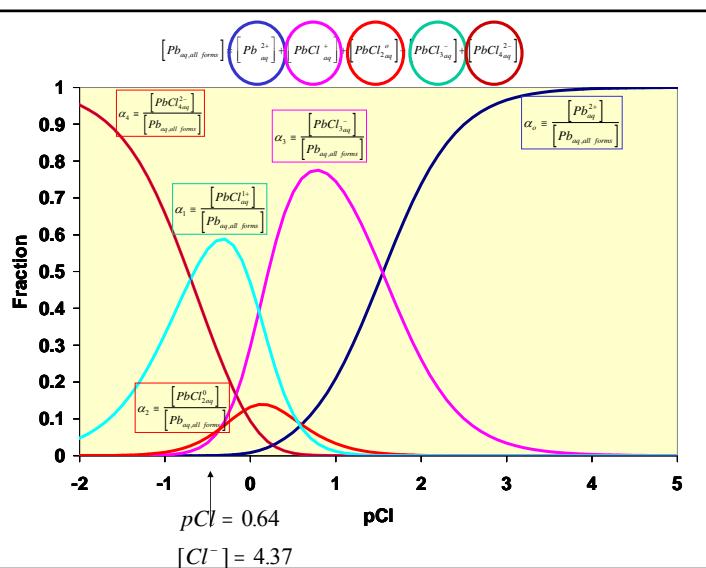


$$K_{f3} \quad K_{f3} = \frac{[PbCl_{3,aq}^{-}]}{[PbCl_{2,aq}^0][Cl_{aq}^{-}]}; \quad \boxed{[PbCl_{3,aq}^{-}] = K_{f3} [PbCl_{2,aq}^0][Cl_{aq}^{-}]}$$



$$K_{f4} \quad \boxed{[PbCl_{4,aq}^{2-}] = K_{f1} K_{f2} K_{f3} K_{f4} [Pb_{aq}^{2+}][Cl_{aq}^{-}][Cl_{aq}^{-}][Cl_{aq}^{-}]}$$

Don't sweat the math
=an example only



Example 2: A complex formed from a ligand and a metal

$$\boxed{[PbCl_{aq}^{+}] = K_{f1} [Pb_{aq}^{2+}][Cl_{aq}^{-}]}$$

$$\boxed{[PbCl_{2,aq}^0] = K_{f2} K_{f1} [Pb_{aq}^{2+}][Cl_{aq}^{-}][Cl_{aq}^{-}]}$$

$$\boxed{[PbCl_{3,aq}^{-}] = K_{f3} K_{f2} K_{f1} [Pb_{aq}^{2+}][Cl_{aq}^{-}][Cl_{aq}^{-}][Cl_{aq}^{-}]}$$

$$\boxed{[PbCl_{4,aq}^{2-}] = K_{f4} K_{f3} K_{f2} K_{f1} [Pb_{aq}^{2+}][Cl_{aq}^{-}][Cl_{aq}^{-}][Cl_{aq}^{-}][Cl_{aq}^{-}]}$$

$$\boxed{[Pb_{aq,all \ forms}] = [Pb_{aq}^{2+}] + [PbCl_{aq}^{+}] + [PbCl_{2,aq}^0] + [PbCl_{3,aq}^{-}] + [PbCl_{4,aq}^{2-}]}$$

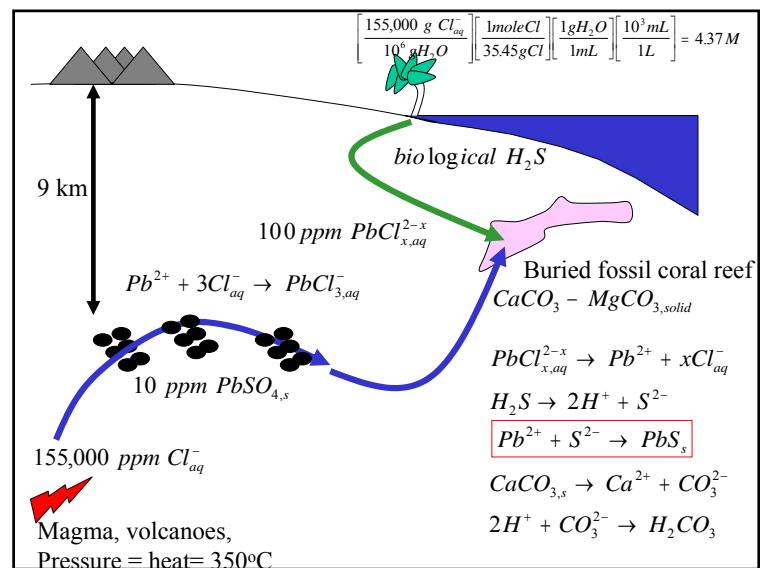
$$\boxed{[Pb_{aq,all \ forms}] = [Pb_{aq}^{2+}] + K_{f1} [Pb_{aq}^{2+}][Cl_{aq}^{-}] + K_{f1} K_{f2} [Pb_{aq}^{2+}][Cl_{aq}^{-}]^2 + K_{f1} K_{f2} K_{f3} [Pb_{aq}^{2+}][Cl_{aq}^{-}]^3 + K_{f1} K_{f2} K_{f3} K_{f4} [Pb_{aq}^{2+}][Cl_{aq}^{-}]^4}$$

$$\boxed{[Pb_{aq,all \ forms}] = [Pb_{aq}^{2+}] \left(1 + K_{f1} [Cl_{aq}^{-}] + K_{f1} K_{f2} [Cl_{aq}^{-}]^2 + K_{f1} K_{f2} K_{f3} [Cl_{aq}^{-}]^3 + K_{f1} K_{f2} K_{f3} K_{f4} [Cl_{aq}^{-}]^4 \right)}$$

$$\alpha_0 = \frac{[Pb_{aq}^{2+}]}{[Pb_{aq,all \ forms}]} = \frac{[Pb_{aq}^{2+}] \left(1 + K_{f1} [Cl_{aq}^{-}] + K_{f1} K_{f2} [Cl_{aq}^{-}]^2 + K_{f1} K_{f2} K_{f3} [Cl_{aq}^{-}]^3 + K_{f1} K_{f2} K_{f3} K_{f4} [Cl_{aq}^{-}]^4 \right)}{[Pb_{aq,all \ forms}]}$$

$$\alpha_0 = \frac{[Pb_{aq}^{2+}]}{[Pb_{aq,all \ forms}]} = \frac{1}{\left(1 + K_{f1} [Cl_{aq}^{-}] + K_{f1} K_{f2} [Cl_{aq}^{-}]^2 + K_{f1} K_{f2} K_{f3} [Cl_{aq}^{-}]^3 + K_{f1} K_{f2} K_{f3} K_{f4} [Cl_{aq}^{-}]^4 \right)}$$

Predicts amt of total Pb as Pb²⁺ based only on [Cl⁻] Same for $\alpha_1, \alpha_2, \alpha_3, \alpha_4$



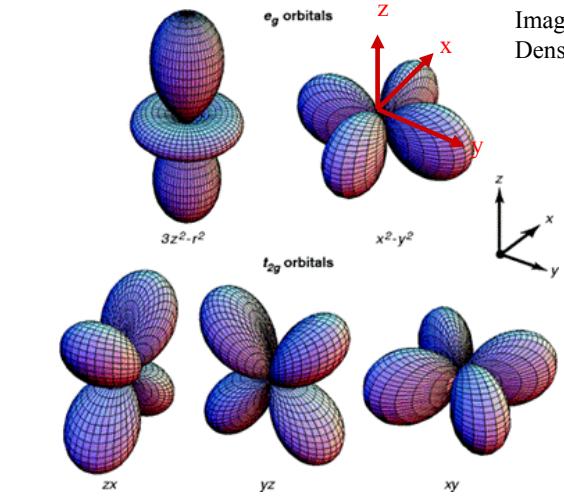
Who is the central atom?

Mostly: Cr, Mn, Fe²⁺, Fe³⁺, Co²⁺, Co³⁺, Ni²⁺, Cu⁺, Cu²⁺, Zn²⁺, Ag⁺

To a lesser extent Al³⁺, Sn²⁺, Hg²⁺, Pb²⁺

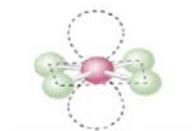
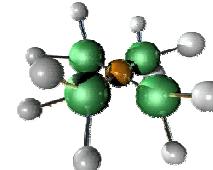
All of these have accessible d orbitals!

Images of electron Density of d orbitals

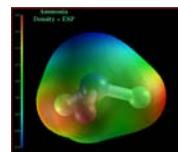


<http://vinobalan.tripod.com/sitebuildercontent/sitebuilderpictures/picture1.gif>

Consider the square planar complex,

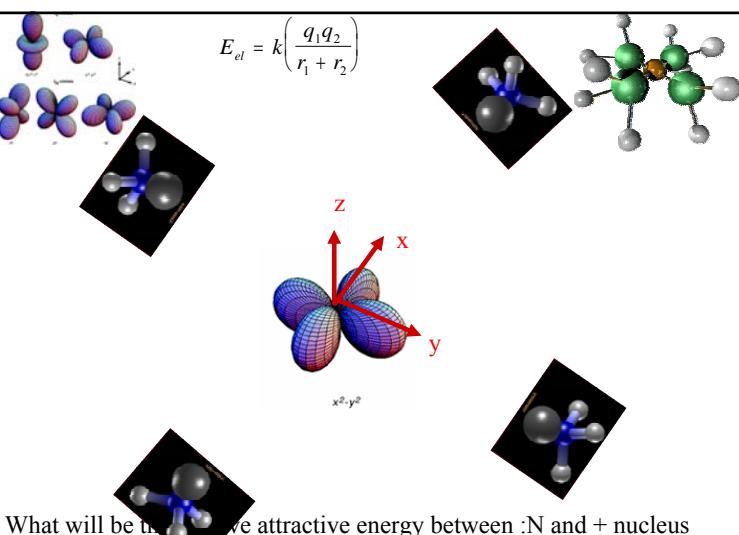


[http://www.uel.education.fr/consultation/reference/chimie/elementspl/apprendre/gcb.elp.fa.101.a2/content/images/cu\(nh3\)4.gif](http://www.uel.education.fr/consultation/reference/chimie/elementspl/apprendre/gcb.elp.fa.101.a2/content/images/cu(nh3)4.gif)
formed from the ability of four incoming electron pairs on NH₃

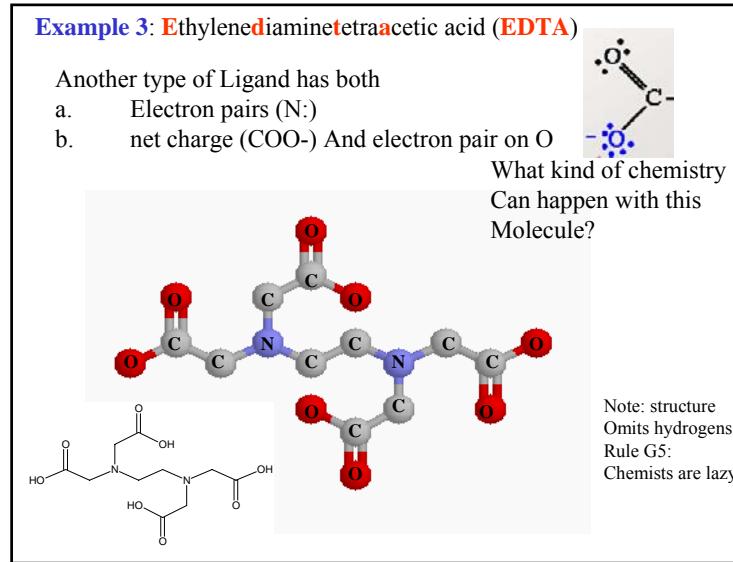
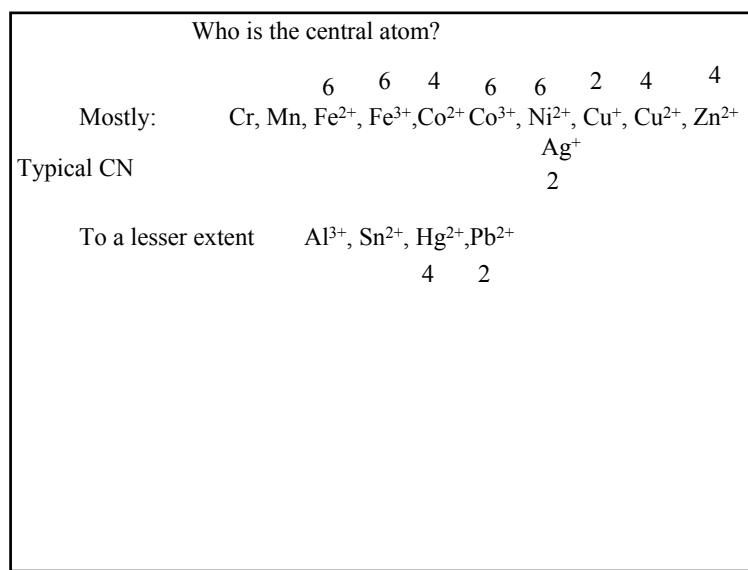
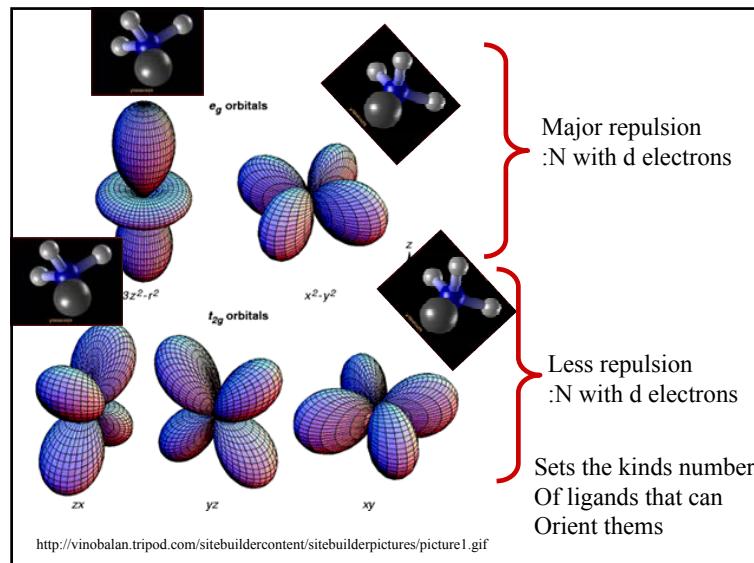
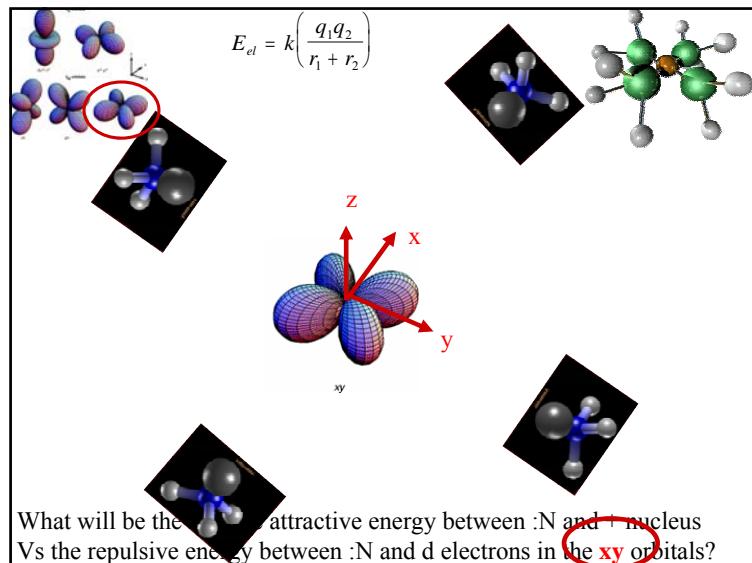


To get very close to the positive nucleus of Cu
Keep in mind Rule C1: It's All about Charge!

$$E_{el} = k \left(\frac{q_1 q_2}{r_1 + r_2} \right)$$

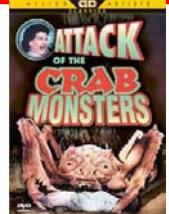


What will be the attractive energy between :N and + nucleus
Vs the repulsive energy between :N and d electrons in the x²-y² orbitals?

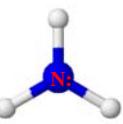


Vocabulary Rules for Coordination Chemistry

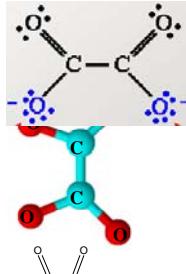
1. Central Atom = cation = Lewis acid
2. Ligands = Lewis Bases
3. Lewis bases have an electron pair which “bites” the metal
 - a. 1 electron pair = **monodentate**
 - b. 2 electron pair = **bidentate**
 - c. > 2 electron pair = **polydentate**



Chelate from Latin from Greek *khele* “claw”
molecular ligand with more than one bond with central metal atom.

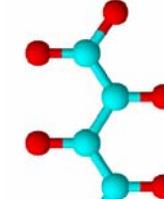


ammonia



oxalate

Rhubarb leaves
From Latin: *oxalis* : wood Sorrel; From Greek *oxus* sour



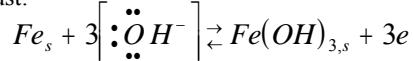
Tartrate
Crystallized wine
From Greek: *tartaron*



citrate
lemons
From Latin: *citron* tree

How Many Teeth on the Following Ligands (Lewis Bases)?

Example 4: Rust:



a red stain on clothing

To remove:

- add lemon juice (citric acid)
- add cream of tartar (tartric acid)
- add oxalic acid

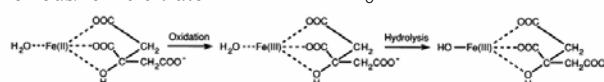
Which will work better:

oxalic acid or citric acid?



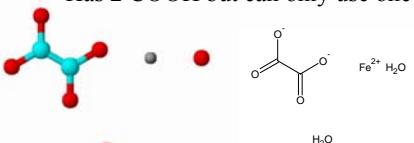
<http://aem.asm.org/cgi/reprint/59/1/109.pdf>

Ferrous/ferric citrate



What is CN of Fe(II)?

Has 2 COOH but can only use one



Uses 2 COOH

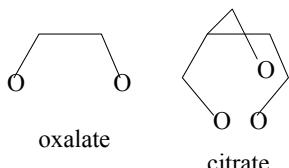
What is CN of Fe(III)?

Ferrous/ferric oxalate

<http://www.chemexper.com/index.shtml?main=http://www.chemexper.com/search/cas/516-03-0.html>

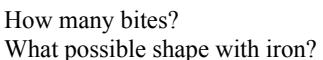
Which of Eloise's hints works better? Oxalic acid or citric acid?

1. Both bites are electron pairs on oxygen
- Compare K_f (formation constants)
- What do you observe?
- How do you explain it?
6. citrate can wrap around Fe^{2+} better.

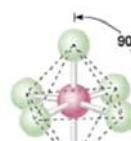
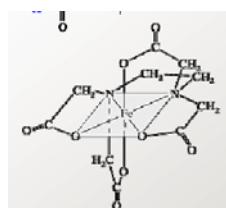
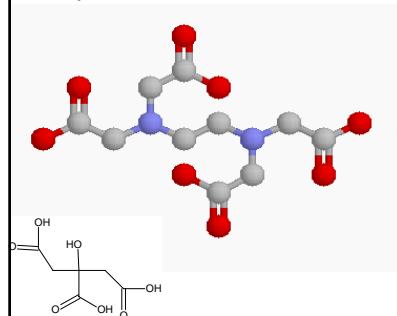


metal	oxalate	citrate
Mg ²⁺	2.8	3.2
Ca ²⁺	3.0	3.2
Fe ²⁺	7.5	11.8
Cu ²⁺	6.2	14.2

Conclusion: **flexibility** is good.



Ethylenediaminetetraacetic acid



AX_6 : octahedron

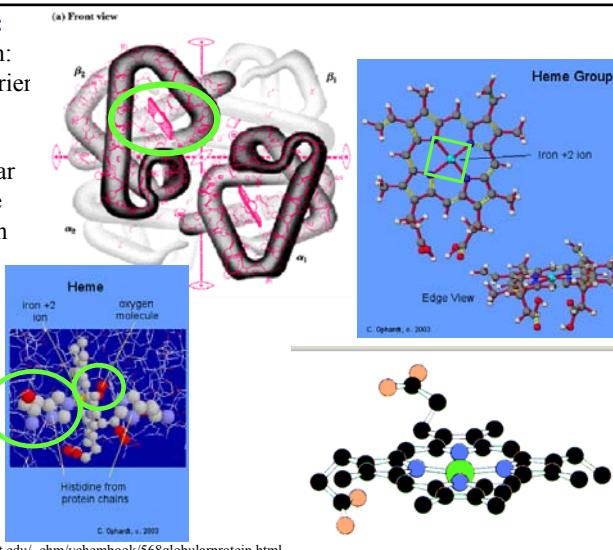
Review Module 10 Covalent bonding

Example 5:

Hemoglobin: Oxygen carrier

Fe is
square planar
with 2 more
coordination
sites
top and
bottom.

One is used for oxygen transport



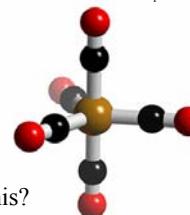
<http://www.elmhurst.edu/~chm/vchembook/568globularprotein.html>

Structure of complex is important

How hemoglobin works (sort of)

Fe²⁺ can have C.N. = 5

Example: $Fe(CO)_5$

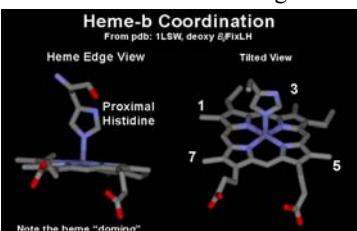


What shape is this?
(Triangular bipyramid)

In deoxygenated hemoglobin it has CN 5, but it is forced
By the shape of the protein to "look like" CN 6 without the 6th ligand

This means that it accepts the 6th Ligand (O_2) (carries oxygen)

But not so strongly. It can easily release it again because it isn't really fully designed to be 6 CN doming



The British Journal of Radiology, 70 (1997), 859-861 © 1997 The British Institute of Radiology

Case report
MRI findings of VIIth cranial nerve involvement in sarcoidosis

M OKI, MD, S TAKIZAWA, MD, PhD, Y OHNUKI, MD and Y SHINOHARA, MD, PhD
 Department of Neurology, Tokai University School of Medicine, Bohseidai, Isehara, Kanagawa, 259-11 Japan

Magnetic Resonance Imaging

Figure 1. Axial image (500/13) demonstrating an extramural iso-signal intensity mass simulating sarcoid at the right internal acoustic canal.

Figure 2. Post-gadolinium, T_1 weighted (500/13) axial image showing markedly enhanced granulomatous lesion (arrow) in the right acoustic canal.

Image Enhancement Shows lesion

Image enhanced By a complex ion

Another Medicinal Example of Complexation

Diethylenetriamine pentaacetic Acid =DTPA

Biomacromolecules 2004, 5, 54-61

Conformation and Structure of Polymeric Contrast Agents for Medical Imaging

E. E. Uzgiris,* Harvey Cline, Bahram Moosseri, Brian Hammond, Mohan Amaralunga, Joanne F. Smith, and Gregory Goddard

Figure 2. Chemical structure of Gd-DTPA-polylysine.

Figure 3. Space-filling representation of the calculated lowest energy structure of Gd-DTPA-polylysine. The complete conjugation of a chain of 69 repeating units of the Rasmussen repeat is shown. This structure is a right-hand helix of pitch 3. Peptide chain is in a horizontal orientation. The DTPA moieties are the spherical structures appended to the peptide backbone through the lysine 4 carbon space and that spiral around the backbone chain as shown.

$Gd^{3+} + DTPA^{3-} \rightleftharpoons Gd(DTPA)$ $K_f = 10^{23}$

Stuff patient with delicious gadolinium-DTPA for MRI imaging

Characteristics of Gadolinium-DTPA Complex: What might you want to know?

TABLE 2: Acute Lethal Toxicity

Agent	Dose (mmol/kg)	No. Deaths/No. Rats	Interpolated LD_{50} (mmol/kg)*
Meglumine diatrizoate	12	0/4	
	20	1/4	18
	28	4/4	
GdCl ₃	0.3	0/5	
	0.45	2/5	0.5
	0.6	5/5	
Meglumine-Gd-EDTA	0.3	2/3	
	1.2	5/5	0.3
Dimegulamine-Gd-DTPA	2.5	0/4	
	7.5	0/4	10
	12.5	4/4	
Na ₃ Ca-DTPA	1	0/6	
	2	2/6	
	4	0/6	
	6	6/6	5

* LD_{50} in male and female rats (90-110 g) after intravenous injection

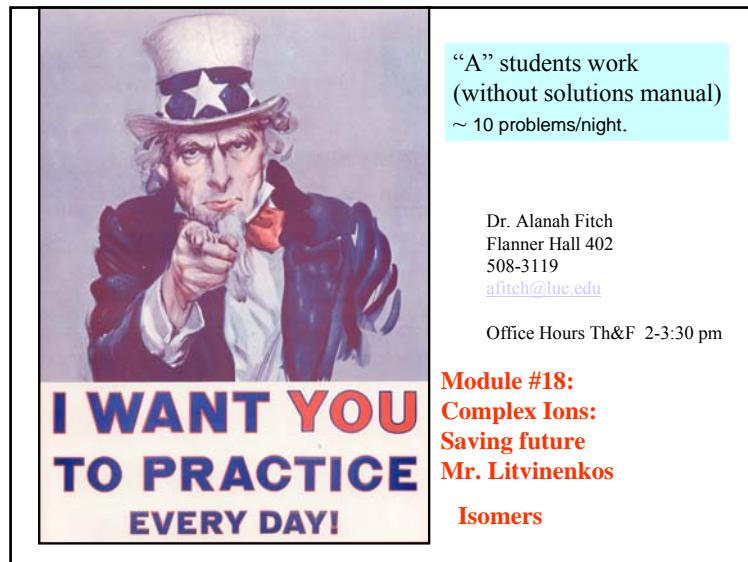
<http://www.ajronline.org/cgi/reprint/142/3/619.pdf>

What is CN for Gd-DTPA? 7

What is most probable structure?

Trick question!
 We never saw any structure With 7!

Figure 2. Chemical structure of Gd-DTPA-polylysine.



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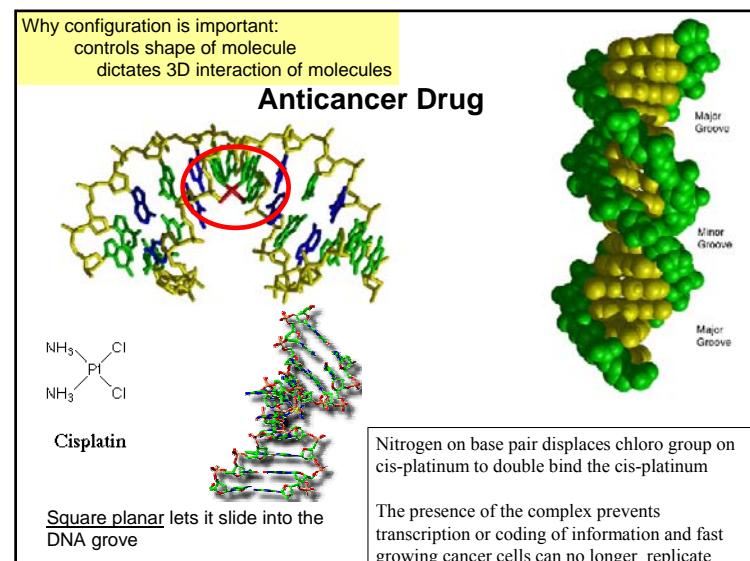
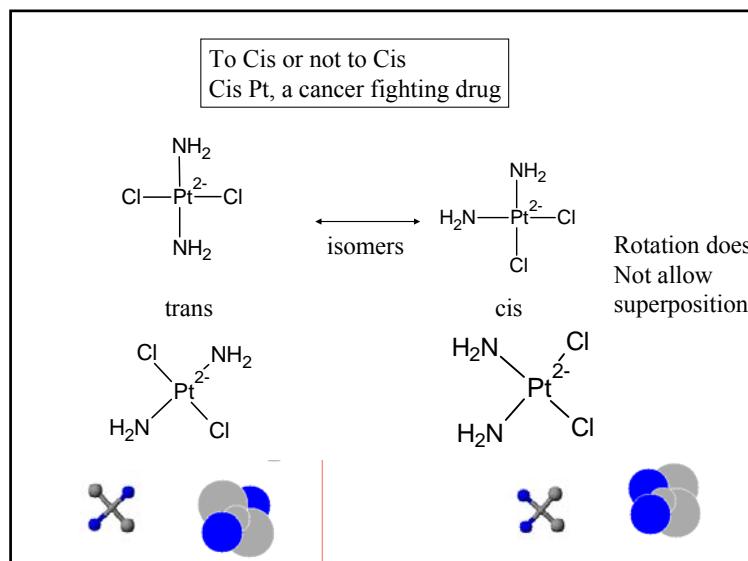
If you can read this you will do well in organic chemistry

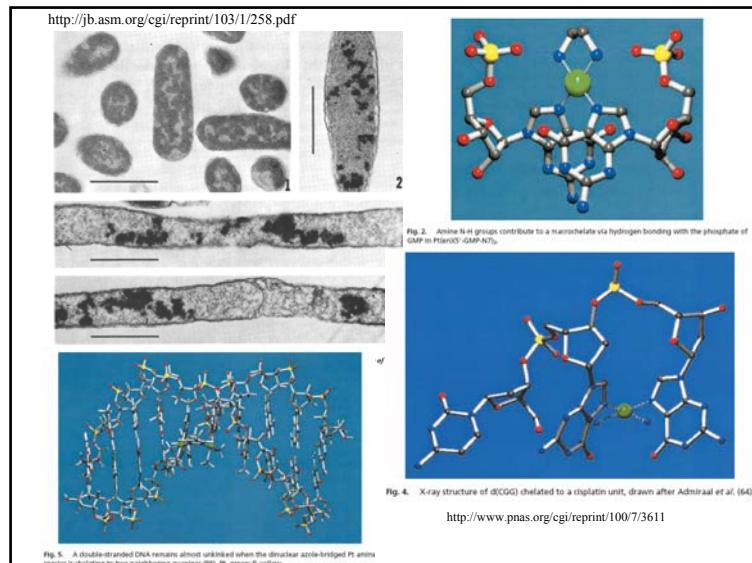
Shapes

A molecule can exist in different **isomers**, which affects its activity.

Several types, but most important are stereoisomers

1.	geometrical cis/trans	Cis= same side Trans = opposite side
2.	optical mirror image: non-superimposable: chiral	

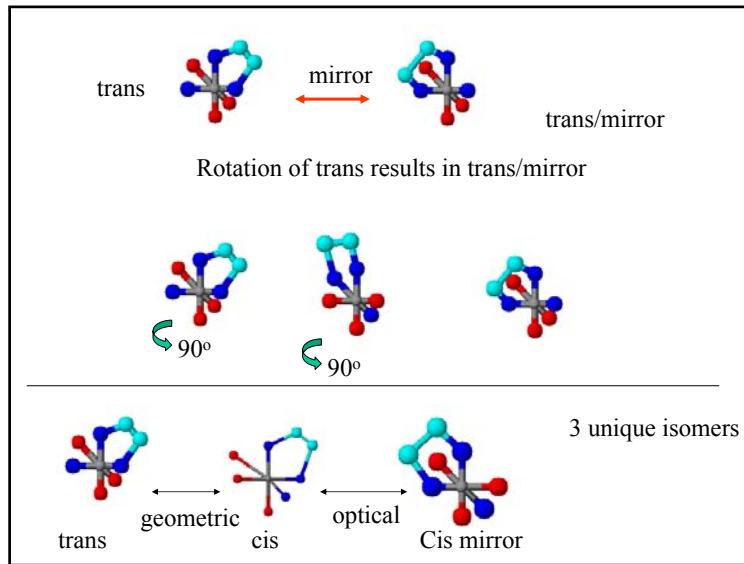
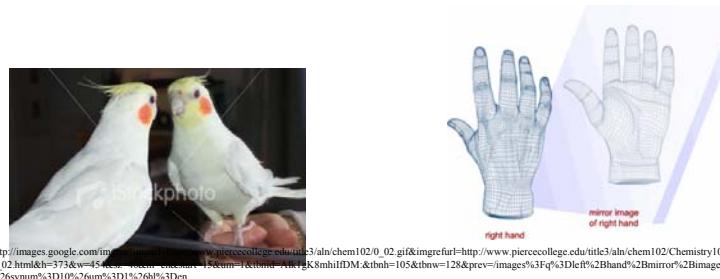




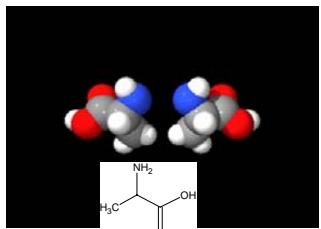
Isomers

Several types, but most important are stereoisomers

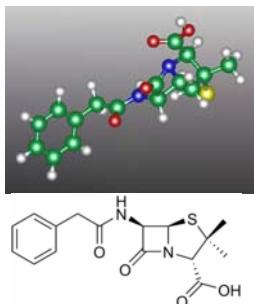
1. geometrical
cis/trans
2. optical
mirror image: non-superimposable: chiral



Why Optical Isomers are important



Wikipedia Alanine: optical isomers



Penicillin's activity is stereoselective.

The antibiotic only works on peptide links of d-alanine which occurs in the cell walls of bacteria – but not in humans. The antibiotic can only kill the bacteria, and not us, because we do not have d-alanine.

To see an animation of the cellular level of how this works:

<http://student.ccbcmd.edu/courses/bio141/lecguide/unit1/prostruct/penres.html>

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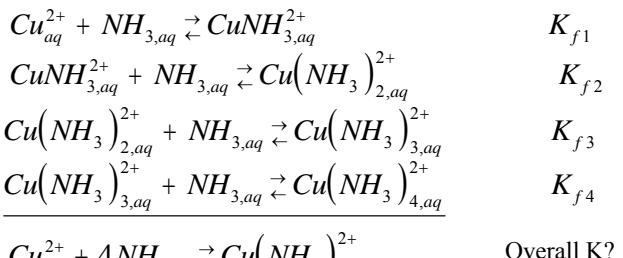
Office Hours Th&F 2-3:30 pm

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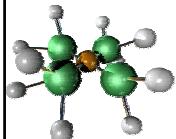
Complexation Constants



**I WANT YOU
TO PRACTICE
EVERY DAY!**



$$K_{rx} = K_{f1} K_{f2} K_{f3} K_{f4} = 2 \times 10^{12}$$



EXAMPLE calculation

At what concentration of ammonia is the divalent cation of copper concentration equal to the copper(II) tetraammine concentration? The overall formation constant for the tetraammine complex is 2×10^{12} . The Pressure is 1 atm.

know	Don't Know	Red Herrings
Reaction	$[NH_3]$	1 atm
$K_f = 2 \times 10^{12}$		
$[Cu^{2+}] = [Cu(NH_3)_4]^{2+}$	$[NH_{3,aq}]^4 = \frac{1}{2 \times 10^{12}}$	
$Cu_{aq}^{2+} + 4NH_{3,aq} \rightleftharpoons Cu(NH_3)_{4,aq}^{2+}$	$[NH_{3,aq}] = \sqrt[4]{\frac{1}{2 \times 10^{12}}} = 8.409 \times 10^{-4}$	
$K_f = 2 \times 10^{12} = \frac{[Cu(NH_3)_{4,aq}^{2+}]}{[Cu_{aq}^{2+}][NH_{3,aq}]^4} = \frac{[Cu(NH_3)_{4,aq}^{2+}]}{[Cu(NH_3)_{4,aq}^{2+}][NH_{3,aq}]^4} = \frac{1}{[NH_{3,aq}]^4}$		

$$K_{rx} = K_{f1}K_{f2}K_{f3}K_{f4}K_{f5}K_{f6}\dots\dots K_{fn}$$

What do you observe?

Lead Complexation

Constants

Ligand	logK1	logK2	LogK3	logK4	logKf
F-	1.4	1.1			2.5
Cl-	1.55	0.6	-0.4	-0.7	1.05
Br-	1.8	0.8	-0.1	-0.3	2.2
I-	1.9	1.3	0.7	0.6	4.5
OH-	6.3	4.6	2		12.9
Acetate	2.7	1.4			4.1
Oxalate	4.9	1.9			6.8
Citrate	5.7				5.7
EDTA	17.9				17.9

Which are polydentate?
What do you observe?

Why so large?

An Example Problem

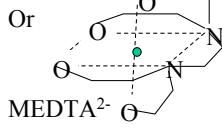
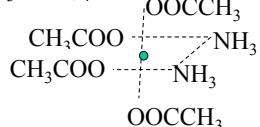
$$\frac{1\mu\text{gPb}}{dL} = \frac{0.04826\mu\text{mol}}{L} = 4.826 \times 10^{-8} \frac{\text{mol}}{L}$$

Children

Symptom	$\mu\text{g/dL}$	M
death	135	6.5×10^{-6}
encephalopathy	90	4.34
frank anemia	70	3.37
colic	60	2.89
decreased hemoglobin synthesis	40	1.93×10^{-6}
decreased Vit. D metabolism	30	1.44
decreased nerve conduction velocity	20	0.97
Decreased IQ, hearing, growth	10	0.48×10^{-6}

$$\frac{1\mu\text{gPb}}{dL} = \frac{1\mu\text{gPb}}{0.1L} = \frac{10^{-6}\text{ gPb}}{(0.1)10^3\text{ gwater}} = \frac{10 \times 10^{-9}\text{ gPb}}{\text{gwater}} = 10\text{ ppb}$$

Can you guess which will have a higher K_f value:



Because all the “bites” are on one ligand, and because they do not have the motional freedom of six individual bites, the probability of having a portion of EDTA on the Lewis Acid metal center is higher than for the individual ligands.

Therefore: $K_f(\text{EDTA}) \gg \gg \gg K_f(\text{six similar ligands})$

Use EDTA to confine metal ions

1. forensic blood sample (O.J. Simpson trial)
2. In food products
3. To purify radioactive metals from water
4. **To treat metal poisoned patients**

EXAMPLE If a 30 kg child comes in with symptoms of colic, seizures, persistent fatigue, and is known to have eaten paints we diagnose lead poisoning. A clinical test shows the child to have 40 $\mu\text{g/dL}$ blood lead. Our first goal is to lower the amount of lead in the blood stream.

Blood volume in an adult is about 4 L. Estimate a blood volume of 3 L in a child. We will need to give this child some mg amount of a ligand to form a complex ion with lead that is soluble so that it can be carried to the kidneys and filtered into urine and removed.

What would be the equilibrium blood lead concentration if we gave the child 28.7 mg CaEDTA/kg weight/day? The molecular weight of CaNa₂EDTA is 374.28. The child is 30 kg, estimated blood volume of 3 L. Estimate EDTA is adsorbed from stomach to blood stream.

What would be the **equilibrium blood lead concentration** if we gave the child 28.7 mg CaEDTA/kg weight/day? The molecular weight of CaNa₂EDTA is 374.28. The child is 30 kg, estimated blood volume of 3 L. Estimate EDTA is adsorbed from stomach to blood stream.

Know	Don't Know
40 ug/dLBlood lead value	molarity blood lead
3 L volume of blood	
28.7 mg EDTA	molarity EDTA
m.w. 374.28	
$K_f = 10^{17.9}$	equil. conc. lead
	$[EDTA_{init}] = \frac{(28.7 \text{ mg EDTA}) \left(\frac{1 \text{ g}}{10^3 \text{ mg}} \right) \left(\frac{1 \text{ mole}}{374.28 \text{ g}} \right)}{3 \text{ L}} = 7.66 \times 10^{-5} \text{ M}$
	$[Pb_{init}] = \left(\frac{40 \mu\text{g Pb}}{dL} \right) \left(\frac{10 \text{ dL}}{L} \right) \left(\frac{1 \text{ mole}}{207.2 \text{ g}} \right) \left(\frac{1 \text{ g}}{10^6 \mu\text{g}} \right) = 1.93 \times 10^{-6} \text{ M}$

What would be the **equilibrium blood lead concentration** if we gave the child 28.7 mg CaEDTA/kg weight/day? The molecular weight of CaNa₂EDTA is 374.28. The child is 30 kg, estimated blood volume of 3 L. Estimate EDTA is adsorbed from stomach to blood stream.

EDTA ⁴⁻	Pb ²⁺	EDTA-Pb ²⁺
sto i 1	1	1
Init 7.66x10 ⁻⁵	1.93x10 ⁻⁶	0
Change -x	-x	+x
Equil 7.44x10 ⁻⁵ -x	1.93x10 ⁻⁶ -x	x

$$K_f = \frac{[PbEDTA_{aq,eq}^{2-}]}{[EDTA_{aq,eq}^{4-}][Pb_{aq,eq}^{2+}]} = \frac{x}{([EDTA_{init}^{4-}] - x)(1.93 \times 10^{-6} - x)}$$

$$K_f ([EDTA_{init}^{4-}] - x)([Pb_{init}] - x) = x$$

$$K_f ([EDTA_{init}^{4-}] [Pb_{init}] - [Pb_{init}]^2 x - [EDTA_{init}^{4-}] x + x^2) = x$$

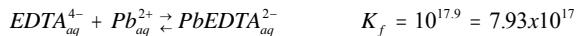
$$K_f [EDTA_{init}^{4-}] [Pb_{init}] - K_f x [Pb_{init}] - K_f x [EDTA_{init}^{4-}] + K_f x^2 = x$$

$$K_f x^2 - K_f x [Pb_{init}] - K_f x [EDTA_{init}^{4-}] + K_f [EDTA_{init}^{4-}] [Pb_{init}] = 0$$

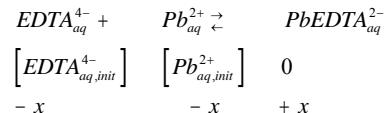
$$\log K_f = 10^{17.9}$$

Is this K value large?
or small?

What does that mean for the extent of the reaction?



What does this mean for the magnitude of change, x, in the reaction?



How will this inform our thinking on how to solve the problem?

2 strategies are possible

1. start with an equilibrium problem
2. first assume a complete reaction $EDTA_{aq}^{4-} + Pb_{aq}^{2+} \rightarrow PbEDTA_{aq}^{2-}$
then calculate dissociation $PbEDTA_{aq}^{2-} \rightleftharpoons EDTA_{aq}^{4-} + Pb_{aq}^{2+}$

$$K_f x^2 - K_f x [Pb_{init}] - K_f x [EDTA_{init}^{4-}] - x + K_f [EDTA_{init}^{4-}] [Pb_{init}] = 0$$

$$K_f x^2 - x (K_f [Pb_{init}] + K_f [EDTA_{init}^{4-}] + 1) + K_f [EDTA_{init}^{4-}] [Pb_{init}] = 0$$

$$a = K_f = 7.943 \times 10^{17}$$

$$b = - (K_f [Pb_{init}] + K_f [EDTA_{init}^{4-}] + 1)$$

$$b = - [(7.93 \times 10^{17})(1.93 \times 10^{-6}) + (7.93 \times 10^{17})(7.66 \times 10^{-5}) + 1] = -6.24 \times 10^{13}$$

$$c = K_f [EDTA_{init}^{4-}] [Pb_{init}] = (7.93 \times 10^{17})(1.93 \times 10^{-6})(7.66 \times 10^{-5}) = 1.17 \times 10^8$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad x = \frac{6.24 \times 10^{13} \pm \sqrt{3.52 \times 10^{27}}}{1.59 \times 10^{18}}$$

$$x = \frac{-(-6.24 \times 10^{13}) \pm \sqrt{(-6.24 \times 10^{13})^2 - 4(7.943 \times 10^{17})(1.17 \times 10^8)}}{2(7.943 \times 10^{17})} \quad x = \frac{6.24 \times 10^{13} \pm 5.93104 \times 10^{13}}{1.59 \times 10^{18}}$$

$$x = \frac{6.24 \times 10^{13} \pm \sqrt{3.89 \times 10^{27} - 3.73 \times 10^{26}}}{1.59 \times 10^{18}}$$

$$x = \frac{6.24 \times 10^{13} \pm 5.93104 \times 10^{13}}{1.59 \times 10^{18}}$$

$$x = 7.66 \times 10^{-5}$$

$$x = 1.93 \times 10^{-6}$$

$$[Pb^{2+}_{eq}] = [Pb^{2+}_{init}] - x = 1.93 \times 10^{-6} - x$$

$$[Pb^{2+}_{eq}] = 1.93 \times 10^{-6} - 7.66 \times 10^{-5} = \text{neg answer}$$

$$[Pb^{2+}_{eq}] = 1.93 \times 10^{-6} - 1.93 \times 10^{-6} = 0$$

Of these two the second
Answer is best,

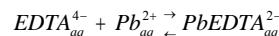
$$x = [Pb^{2+}_{aq}] = 3.17 \times 10^{-20} M = 6.79 \times 10^{-13} \frac{\mu g}{dL}$$

$$[Pb^{2+}_{eq}] = 0$$

$$[PbEDTA^{2-}_{de}] = 1.93 \times 10^{-6}$$

$$[EDTA^{4-}_{eq}] = [EDTA^{4-}_{init}] - 1.93 \times 10^{-6} = 7.66 \times 10^{-5} - 1.93 \times 10^{-6} = 7.467 \times 10^{-5}$$

No conc. is ever exactly zero.
This is a case where we
should've started by considering



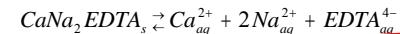
$$7.467 \times 10^{-5} \quad 0 \quad 1.93 \times 10^{-6}$$

$$+ x \quad + x \quad - x$$

In the next 2 slides
(which may
be skipped) x is solved.

What would be the **equilibrium blood lead concentration** if we gave the child 28.7 mg CaEDTA/kg weight/day? The molecular weight of CaNa₂EDTA is 374.28. The child is 30 kg, estimated blood volume of 3 L. Estimate EDTA is adsorbed from stomach to blood stream.

$$[EDTA_{init}] = 7.66 \times 10^{-5} M \quad [Pb_{init}] = 1.93 \times 10^{-6} M$$



$$EDTA^{4-}_{aq} + Pb^{2+}_{aq} \rightleftharpoons PbEDTA^{2-}_{aq} \quad K_f = 10^{17.9} = 7.93 \times 10^{17}$$

So large – complete reaction

$$\text{From EDTA} \quad (7.66 \times 10^{-5} M)(3L) = 3.20 \times 10^{-4} \text{ mole}_{PbEDTA}$$

$$\text{From Pb} \quad (1.93 \times 10^{-6} M)(3L) = 5.79 \times 10 \times 10^{-6} \text{ mole}_{PbEDTA} \text{ Limiting Reagent}$$

$$[EDTA_{after L.R.}] = \frac{3.20 \times 10^{-4} - 5.79 \times 10^{-6}}{3L} = 7.467 \times 10^{-5} \quad [Pb_{after L.R.}] = 0$$

$$[PbEDTA_{after L.R.}] = \frac{5.79 \times 10^{-6}}{3L} = 1.937 \times 10^{-6}$$

What would be the **equilibrium blood lead concentration** if we gave the child 28.7 mg CaEDTA/kg weight/day? The molecular weight of CaNa₂EDTA is 374.28. The child is 30 kg, estimated blood volume of 3 L. Estimate EDTA is adsorbed from stomach to blood stream.

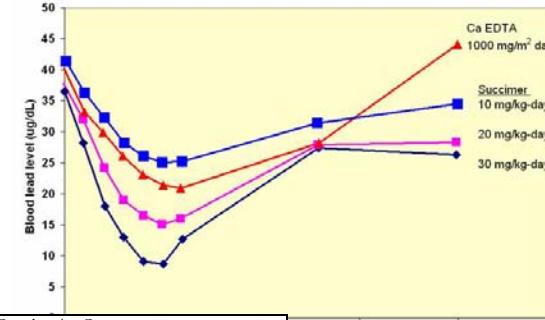
	EDTA ⁴⁻	Pb ²⁺	EDTA-Pb ²⁺
sto	1	1	1
Init	7.44 × 10 ⁻⁵	0	1.93 × 10 ⁻⁶
Change	+x	x	-x
Equil	7.44 × 10 ⁻⁵	x	1.93 × 10 ⁻⁶
Assume	x << 7.44 × 10 ⁻⁵		x << 1.93 × 10 ⁻⁶

$$K_f = 7.93 \times 10^{17} = \frac{[PbEDTA^{2-}_{aq, eq}]}{[EDTA^{4-}_{aq, eq}][Pb^{2+}_{aq, eq}]} = \frac{[PbEDTA^{2-}_{after L.R.}] - x}{([EDTA^{4-}_{after L.R.}] + x)x} \approx \frac{[PbEDTA^{2-}_{after L.R.}]}{([EDTA^{4-}_{after L.R.}] + x)x}$$

$$x = \frac{[PbEDTA^{2-}_{after L.R.}]}{([EDTA^{4-}_{after L.R.}] + x)x} = \frac{1.93 \times 10^{-6}}{(7.44 \times 10^{-5})7.93 \times 10^{17}} = 3.17 \times 10^{-20}$$

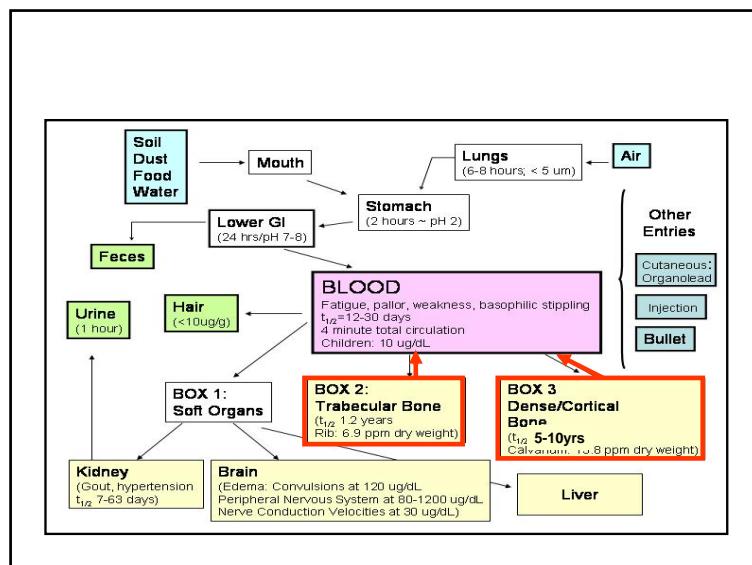
$$x = 3.17 \times 10^{-20} M = 6.79 \times 10^{-13} \frac{\mu g}{dL}$$

Blood lead level actually increases when using EDTA Why?



Ligand	logK1	logK2	logK3	logK4	logKf
F ⁻	1.4	1.1			2.5
Cl ⁻	1.55	0.6	-0.4	-0.7	1.05
Br ⁻	1.8	0.8	-0.1	-0.3	2.2
I ⁻	1.9	1.3	0.7	0.6	4.5
OH ⁻	6.3	4.6	2		12.9
Acetate	2.7	1.4			4.1
Oxalate	4.9	1.9			6.8
Citrate	5.7				5.7
EDTA	17.9				17.9

The constant is very large
For lead – complete reaction
(as we just found out!)
Will search for and mobilize
Other forms of lead



Essentially EDTA is on a search and destroy mission to remove lead.

Any other problems?

Why isn't this therapy the best one medically?

Metal	EDTA
Pb ²⁺	17.9
Fe ²⁺	14.4
Fe ³⁺	25.1
Cu ²⁺	18.8
Zn ²⁺	16.5

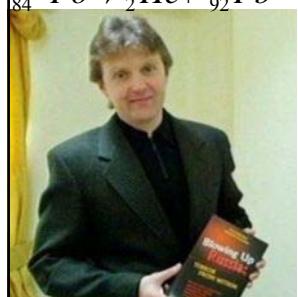
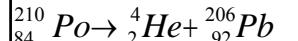
ALAD helps construct the Porphyrin ring for hemoglobin. Zn²⁺ helps in its functioning

Removes other essential Metals; some imp. For structure



An Example of rate constants in the real world: context and calculations

Toxicology of Radioactive Exposure



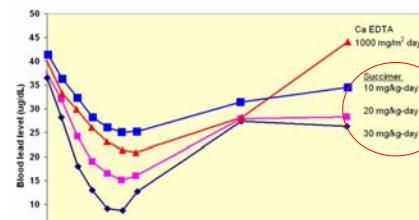
Alexander Litvinenko, former Russian KGB agent poisoned with Polonium on Nov. 1, died Nov. 23, 2006



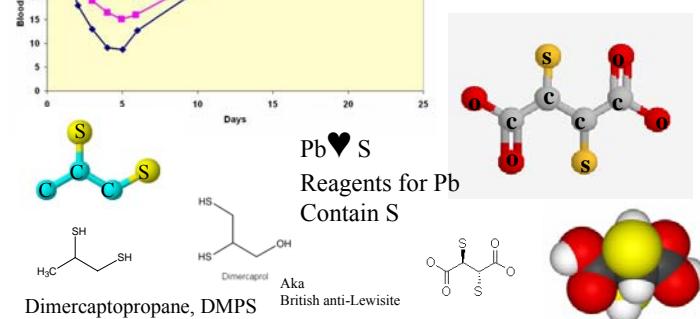
190 ng dose suspected
Could Po be Removed using Complexation reactions?

YES!!

Complexation of Po and Pb for medical treatment



Alternative is "succimer"
Trade name for Dimercaptosuccinic acid, DMSA



Titre du document / Document title**Combined chelation treatment for polonium after simulated wound contamination in rat****Auteur(s) / Author(s)**

VOLF V. (1) ; RENCOVA J. ; JONES M. M. ; SINGH P. K. ;

Affiliation(s) du ou des auteurs / Author(s) Affiliation(s)

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Résumé / Abstract

Contaminated puncture wounds were simulated in rat by intramuscular injection of $[210]\text{Po}$. The aim of the study was to determine the effectiveness of chelation treatment as a function of time, dosage, and route of chelate administration. Ten newly synthesized substances containing vicinal sulphhydryl and carbodithioate groups were used and their effect was compared with that of chelators clinically applicable in man-BAL (2,3-dimercaptopropane-1-ol), DMPS (2,3-dimercaptopropane-1-sulphonate), DMSA (meso-2,3-dimercaptosuccinic acid), and DDTc (sodium diethylamine-N-carbodithioate). The results indicate first that complete removal of $[210]\text{Po}$ from the injection site is achieved by only two local injections of DMPS, beginning as late as 2 h after injection of $[210]\text{Po}$. Second, many of the substances used merely induce translocation of $[210]\text{Po}$ from the injection site into other tissues. Third, a combined local treatment at the injection site with DMPS plus repeated systemic, subcutaneous, treatments with HOEtTC (N,N'-di-(2-hydroxyethyl)ethylenediamine-N,N'-biscarbodithioate), a derivative of DDTc, results after 2 weeks in a reduction of the estimated total body retention of $[210]\text{Po}$ to about one-third of that in untreated controls. In the latter case the cumulative excretion of $[210]\text{Po}$ increased from 8 to 54%, mainly via the faeces.

Revue / Journal Title

International journal of radiation biology (Int. j. radiat. biol.) ISSN 0955-3002

Source / Source

1995, vol. 68, no4, pp. 395-404 (19 ref.)

Titre du document / Document title**Mobilization and detoxification of polonium-210 in rats by 2,3-dimercaptosuccinic acid and its derivatives****Auteur(s) / Author(s)**

RENCOVA J. (1) ; VOLF V. (1) ; JONES M. M. (2) ; SINGH P. K. (2) ;

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(2) Vanderbilt University, Department of Chemistry, PO Box 1583, Nashville, Tennessee 37235, ETATS-UNIS

Résumé / Abstract

Purpose: To reduce retention and toxicity of the alpha particle emitter polonium-210 in rats by newly developed chelating agents. Materials and methods: Repeated subcutaneous chelation was conducted after intravenous injection of $[210]\text{Po}$ nitrate. For reduction of $[210]\text{Po}$ retention the treatment with vicinal di thiols meso- and rac-2,3-dimercaptosuccinic acid (DMSA), mono-i-amylneso-2,3-dimercapto succinate (Mi-ADMS) and mono-N-(i-butyl)-meso-2,3-dimercapto succinamide (Mi-BDMA) were used. For the reduction of toxic effects of $[210]\text{Po}$, treatment effectiveness of Mi-BDMA was compared with that of N,N'-di(2-hydroxyethyl)ethylenediamine-N,N'-biscarbodithioate (HO-EtTC, reference compound). Results: Treatment with meso-DMSA and rac-DMSA altered the main excretion route of $[210]\text{Po}$, reduced its contents in the liver but increased its deposition in the kidneys. Treatment with Mi-ADMS or Mi-BDMA increased total excretion of $[210]\text{Po}$, mainly via the faeces. Only Mi-BDMA decreased $[210]\text{Po}$ levels in the kidneys. The effectiveness of all chelators decreased with delay in the start of treatment. In a survival study, the lives of rats treated early with Mi-BDMA or delayed with HOEtTC were prolonged three-fold when compared with rats receiving a lethal amount of $[210]\text{Po}$ only. Conclusions: Of the vicinal di thiols examined, Mi-BDMA was the best mobilizing chelating agent for $[210]\text{Po}$ and it reduced $[210]\text{Po}$ toxicity when the treatment started immediately. However, the detoxification efficacy of the immediate treatment with HOEtTC, observed in our previous study, was superior to that of the present result with Mi-BDMA.

Revue / Journal Title

International journal of radiation biology (Int. j. radiat. biol.) ISSN 0955-3002

Source / Source

2000, vol. 76, no10, pp. 1409-1415 (21 ref.)



“A” students work
(without solutions manual)
~ 10 problems/night.

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Module #18:
Complex Ions:
Saving future
Mr. Litvinenkos

What you need to know

What you need to know

1. Ions and elements likely to be ligands
2. Types of structures likely to be chelates
3. Coordination number
4. Which suggests structure
5. Which suggests isomers, geometric and stereo (mirror)
6. Why chelates have larger K_f
7. Equilibrium calculation using K_f
8. Know what a “large K_f ” is
9. Interpret a diagram of fractional complexation vs $p(\text{ligand})$
10. Explain how that diagram helps you plan for qualitative analysis (e.g. your current 101 labs)
11. Explain one of the four examples of complexation in biology
or
One of one examples of complexation in geochemistry

