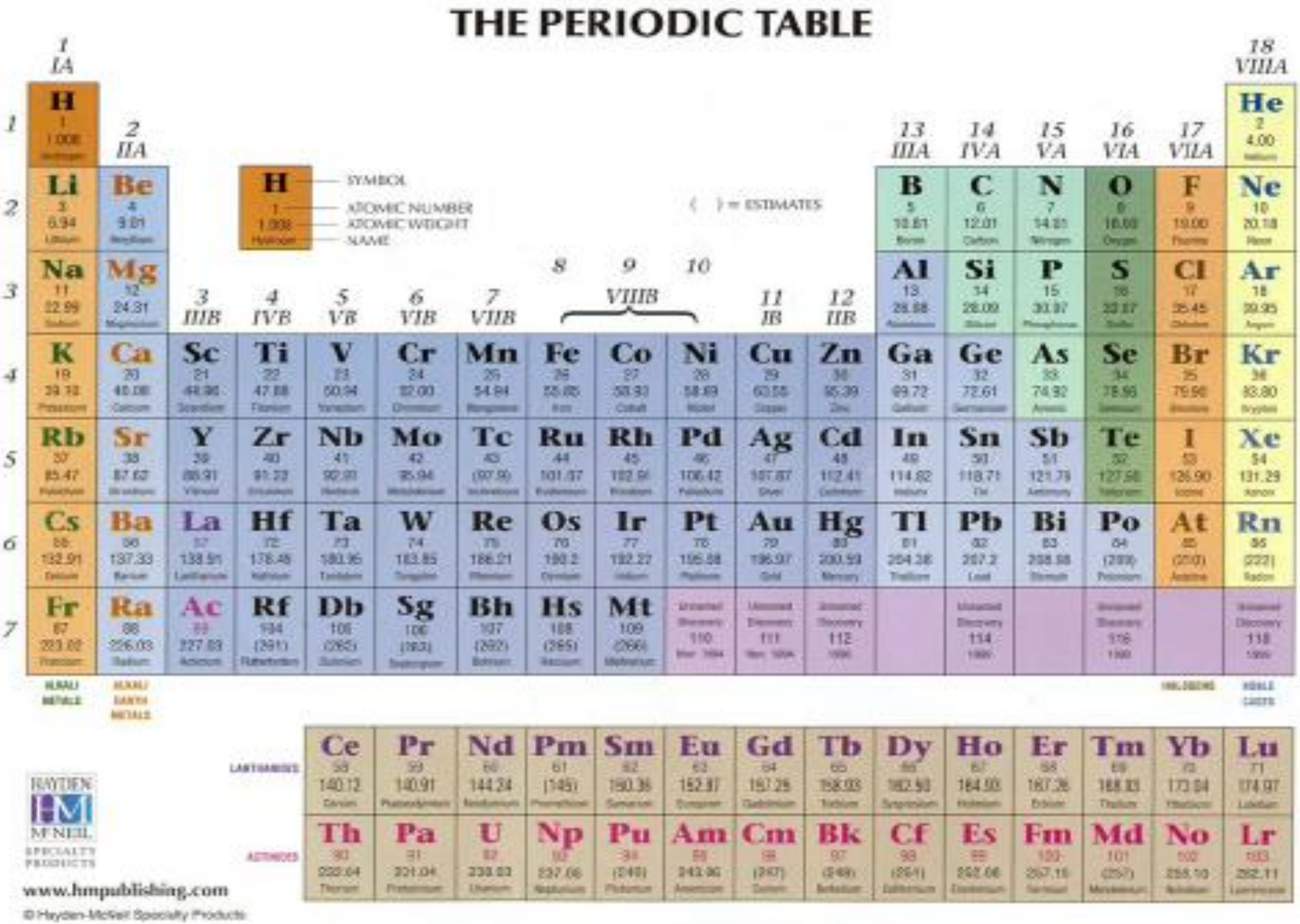
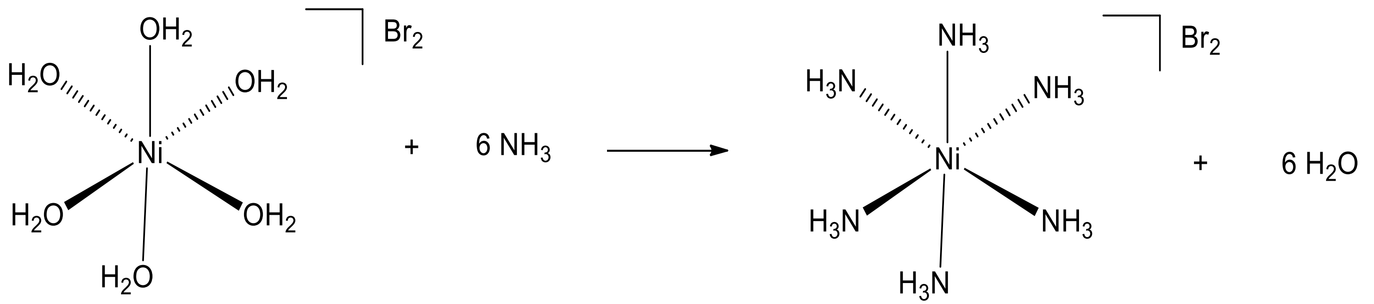

THE PERIODIC TABLE
SYMBOL
ATOMIC NUMBER
ATOMIC WEIGHT
NAME
( ) = ESTIMATES
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac Rf Db Sg Bh Hs Mt
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
www.hmpublishing.com

Week 6

Review of Chapter 2

Ligand substitution reactions and formation constants



$$M + L \rightleftharpoons ML \qquad K^f_1 = \frac{[ML]}{[M]\cdot[L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad K^f_2 = \frac{[ML_2]}{[ML]\cdot[L]}$$

....

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad K^f_n = \frac{[ML_n]}{[ML_{n-1}]\cdot[L]}$$

$$M + nL \rightleftharpoons ML_n \qquad \beta_n = \frac{[ML_n]}{[M][L]^n} = K_1^f \cdot K_2^f \cdots K_n^f$$

K_f tells us:
Which way the reaction proceeds
Which product is more stable

Formation constants of Ni^{2+} ammines, $[Ni(NH_3)_n(OH_2)_{6-n}]^{2+}$

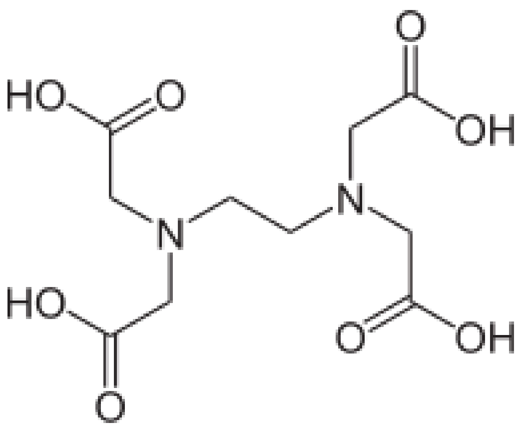
n	pK_n	K_n	K_n/K_{n-1}
1	-2.72	524.8	
2	-2.17	147.9	0.28
3	-1.66	45.71	0.53
4	-1.12	13.18	0.56
5	-0.67	4.677	0.53
6	-0.03	1.07	0.42

$K_1 > K_2 > K_3 > K_4 > K_5 > K_6$

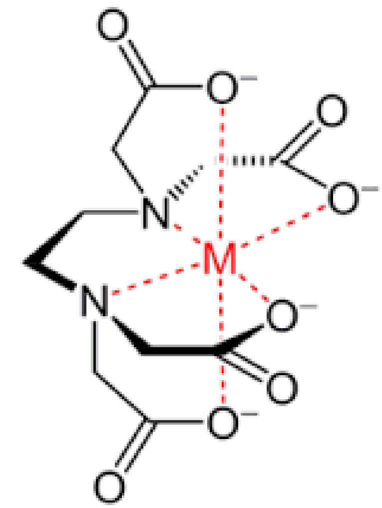
Kn is usually expressed as pK_n

Formation constants of K^f_1 for various metal-EDTA complexes

$$[M(H_2O)_6]^{n+} + EDTA \rightleftharpoons [M(EDTA)]^{n+} + 6\ H_2O$$



Metal ions	Log (K_1^f)
Ag^{+}	7.3
Ca^{2+}	10.8
Cu^{2+}	18.7
Ni^{2+}	18.6
Fe^{2+}	14.3
Fe^{3+}	25.1
Co^{2+}	16.1
Co^{3+}	36.0
V^{2+}	12.7
V^{3+}	25.9



Take home messages:

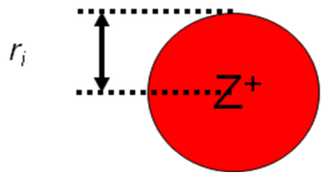
- Very large K_f value indicates reactants are used up
- EDTA complex is extremely stable relative to water complex
- Charge density of metal goes up so does K_f
- Indicates relative differences in stability of complexes

DG° = -RTlnK, R = 8.31 J K^{-1} mol^{-1}

$\Delta G^o = \Delta H^o - T\Delta S^o$ enthalpic stabilization or entropic stabilization

How to determine the relative differences in stability in complexes

1) Charge and size of metals (charge density) – electrostatic interactions of spherical metals and ligands



- higher the Z^2/r_i typically the larger the K_f
- Applies to hard spherical ligands and metals

2) Irving Williams Series – for first row transition metals in a 2+ oxidation state

Ionic radii

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

$Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} < Cu^{2+} < Zn^{2}$

According to Irving Williams Series

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

3) Classification of metal and ligand with regard to hard soft acid base chemistry

Ralph Pearson's Hard Soft Acid Base Theory

Table showing the nature of ligands and metals

Hard (Class A)	Intermediate	Soft (Class B)
Ligands		
F^-, O^{2-}, ^-OH, OH_2, OHR, $RCOO^-$, NH_3, NR_3, RCN, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}	Br^-, ^-SR, NO_2^-, N_3^-, SCN^-, H_5C_5N	PR_3, SR_2, SeR_2, AsR_3, CNR, CN^-, SCN^-, CO, I^-, H^-, R^-
Metal Ions		
Mo^{5+}, Ti^{4+}, V^{4+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Al^{3+}, Eu^{3+}, Cr^{2+}, Mn^{2+}, Ca^{2+}, Mg^{2+}, Be^{2+}, K^+, Na^+, Li^+, H^+	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}	Cu^+, Rh^+, Ag^+, Au^+, Pd^{2+}, Pt^{2+}, Hg^{2+}, Cd^{2+}

Table showing the nature of ligands as you go down the periodic chart.

Complexes of *Class A* Metal Ions	Ligands			Complexes of *Class B* Metal Ions
strongest ↓	R_3N	R_2O	F^-	weakest ↑
	R_3P	R_2S	Cl^-	
	R_3As	R_2Se	Br^-	
weakest	R_3Sb	R_2Te	I^-	strongest

Trends:

a. **Hard metals:** high oxidation states > 2 and early transition metals

b. **Soft metals:** late transition metals and low-oxidation states

c. **Intermediate metals:** first-row and 2+ oxidation state

d. **Hard ligands:** ligands with donors that are N, O, or halides.

e. **Soft ligands:** are carbon donors or elements found in the second or later rows of the p-block

f. Polarizability and hence softness increases going down the periodic chart.

If a mixture of CO and NH_3 is added to a solution containing Fe(0), which ligand will preferentially bind to Fe?

A. CO

B. NH_3

If a mixture of CO and NH_3 is added to a solution containing Fe(III), which ligand will preferentially bind to Fe?

A. CO
B. NH_3

One reaction favors products and one reaction favors reactants. State which reaction favors products; explain your answer.

A. $[CH_3Hg(H_2O)]^+ + HCl \rightleftharpoons CH_3HgCl + H_3O^+$

B. $[CH_3Hg(H_2O)]^+ + HF \rightleftharpoons CH_3HgF + H_3O^+$

A. Reaction A

B. Reaction B

One reaction favors products and one reaction favors reactants. State which reaction favors products; explain your answer.

A. $[CH_3Hg(H_2O)]^+ + HCl \rightleftharpoons CH_3HgCl + H_3O^+$ $K = 1.8 \times 10^{12}$ and $\log K = 12.25$

B. $[CH_3Hg(H_2O)]^+ + HF \rightleftharpoons CH_3HgF + H_3O^+$ $K = 4.5 \times 10^{-2}$ and $\log K = -1.35$

What do you expect the trend to look like for Co^{3+} and I-, Br-, Cl-, and F-. Please rank the complexes formed in the order of stability.

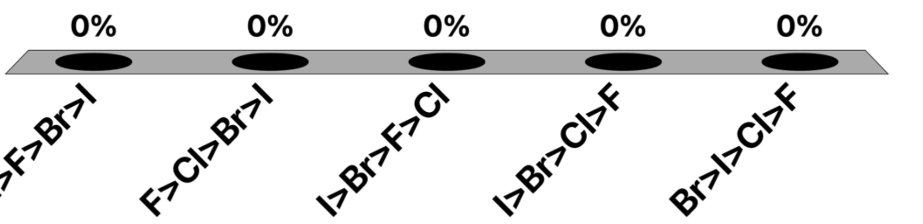
A. Cl>F>Br>I

B. F>Cl>Br>I

C. I>Br>F>Cl

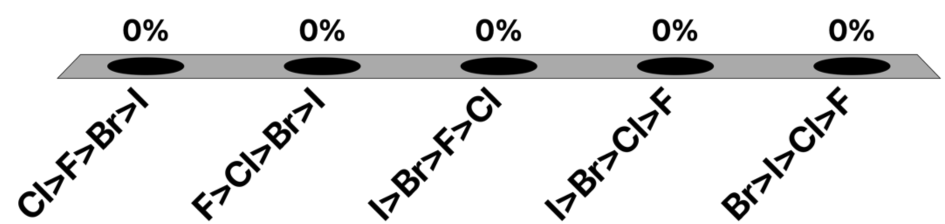
D. I>Br>Cl>F

E. Br>I>Cl>F



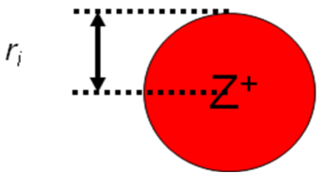
What do you expect the trend to look like for Ag^+ and I^-, Br^-, Cl^-, and F^-. Please rank the complexes formed in the order of stability.

A. Cl>F>Br>I
B. F>Cl>Br>I
C. I>Br>F>Cl
D. I>Br>Cl>F
E. Br>I>Cl>F



How to determine the relative differences in stability in complexes

1) Charge and size of metals (charge density) – electrostatic interactions of spherical metals and ligands



- higher the Z^2/r_i typically the larger the K_f
- Applies to hard spherical ligands and metals

2) Irving Williams Series – for first row transition metals in a 2+ oxidation state

Ionic radii

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

$Mn^{2+} > Fe^{2+} > Co^{2+} > Ni^{2+} < Cu^{2+} < Zn^{2}$

According to Irving Williams Series

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

3) Classification of metal and ligand with regard to hard soft acid base chemistry

4) Strength of ligand as a **Bronsted base** - accepts H+ -

5) Structural Aspects of ligands

   i. Chelate effects

   ii. Size of chelate rings

   iii. Steric effects of ligands

   iv. Macrocyclic effect

How Bronsted basicity influences the stability of complexes

The stronger the Bronsted Basicity (ability to accept a H^+ and hence hard M cations) or the weaker the Bronsted Acidity **the more stable the complex with regard to hard** (class A) **metals**. The opposite is observed for soft metals, i.e. Ag^+, as indicated by the log of the K_f in ().

Stability of Ag^+ complex F^- (0.3) < Cl^- (3.3) < Br^- (4.5) < I^-(8.0)

Acid strength HF < HCl < HBr < HI

PK_a HF > HCl > HBr > HI

Exercise: what do you expect the trend to look like for Co^{3+}?

Answer: The opposite trend observed for Ag^+ b/c Co^{3+} is hard.

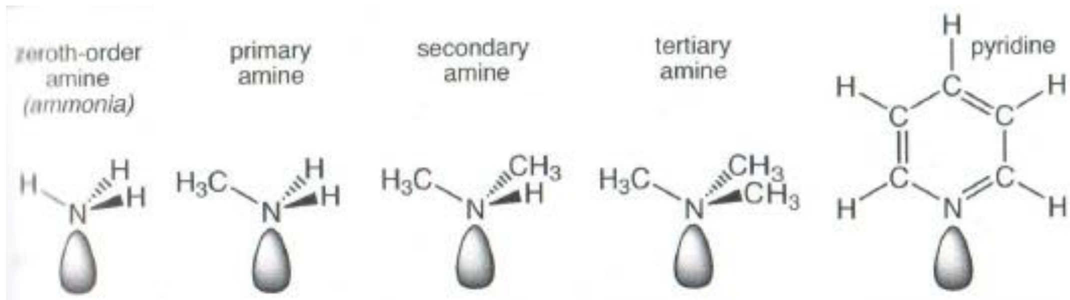
Acid dissociation constant

The acid dissociation constant for $HA \longrightarrow H^+ + A^-$ $\quad PK_a = -\log\frac{[H+][A-]}{[HA]}$

as such the lower the pK_a, the stronger the acid and hence the weaker the conjugate base.

Rule: Ligands with higher PK_a's tend to form stronger complexes with hard metals.

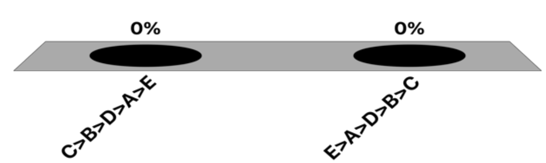
From the PK_as of the conjugate acids, rank the following ligands in terms of their acid strength!



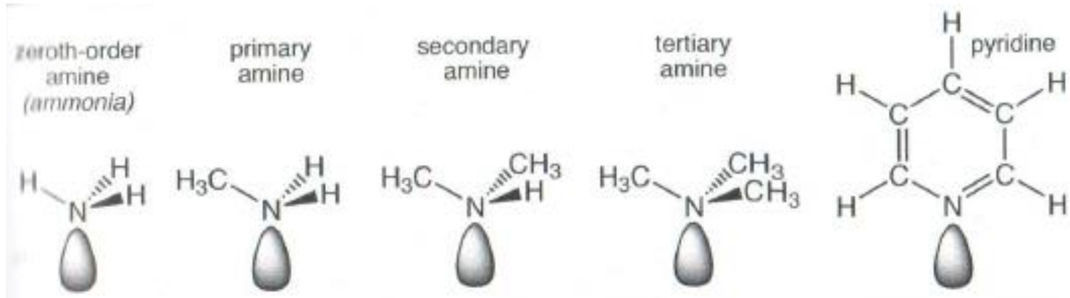
Pka = 9.26	10.66	10.73	9.81	5.25
A	B	C	D	E

A. C>B>D>A>E

B. E>A>D>B>C



Based on what we just learned, which ligands do you think will form the strongest complex with Co^{3+}? Please rank them.

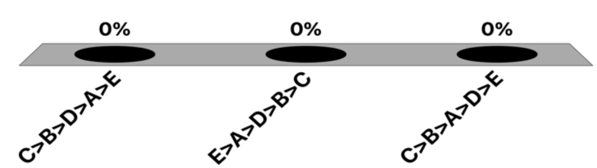


Pka = 9.26	10.66	10.73	9.81	5.25
A	B	C	D	E

A. C>B>D>A>E

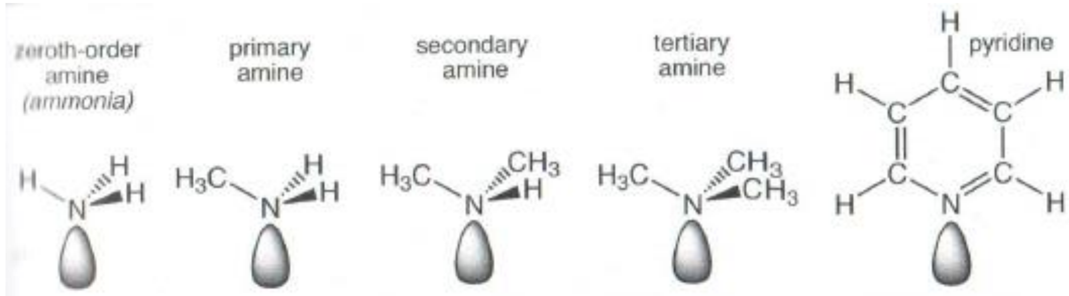
B. E>A>D>B>C

C. C>B>A>D>E



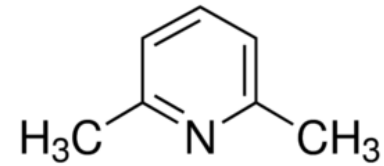
Exercise: From the Pkas of the congugate acids, rank the following ligands in terms of their acid strength!

A **B** **C** **D** **E**



Pka = 9.26 10.66 10.73 9.81 5.25

Answer: E > A > D > B > C



Pka = 6.6

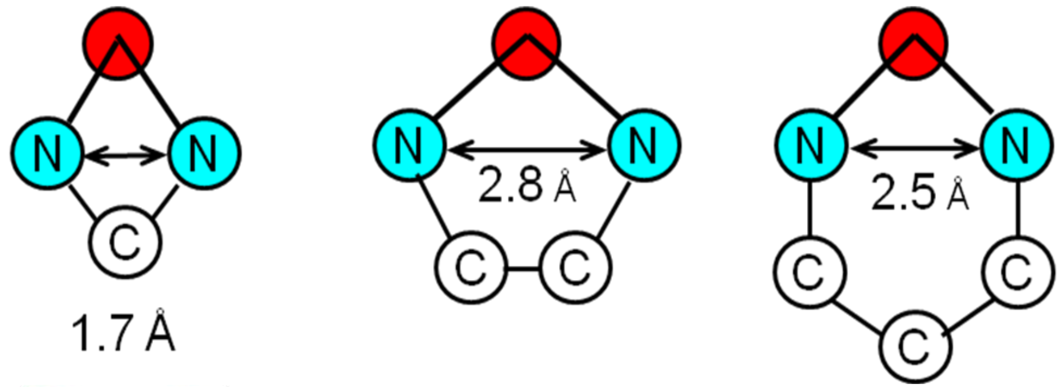
Exercise: Based on what we just learned, which ligand do you think will form the strongest complex with Co^{3+}? Rank them.

Answer: C > B > A > D > E

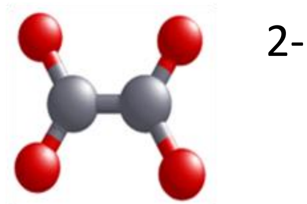
Exercise: Can anyone guess why this is the trend for the acidity with regard to the ammonia and the primary, secondary, and tertiary amines?

Answer: Sterically bulky ligands can counteract bases strength. This is reflected in the decrease in the PK_a for the tertiary amine, which leads to a less stable complex.

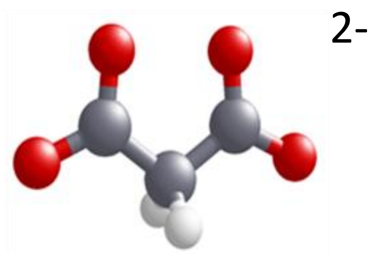
Improved stability in 5-membered rings: The chelate effect



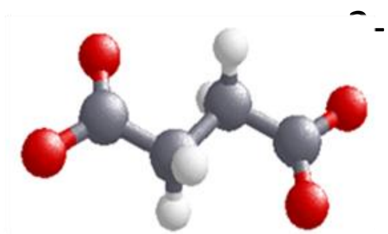
5-membered
oxalato

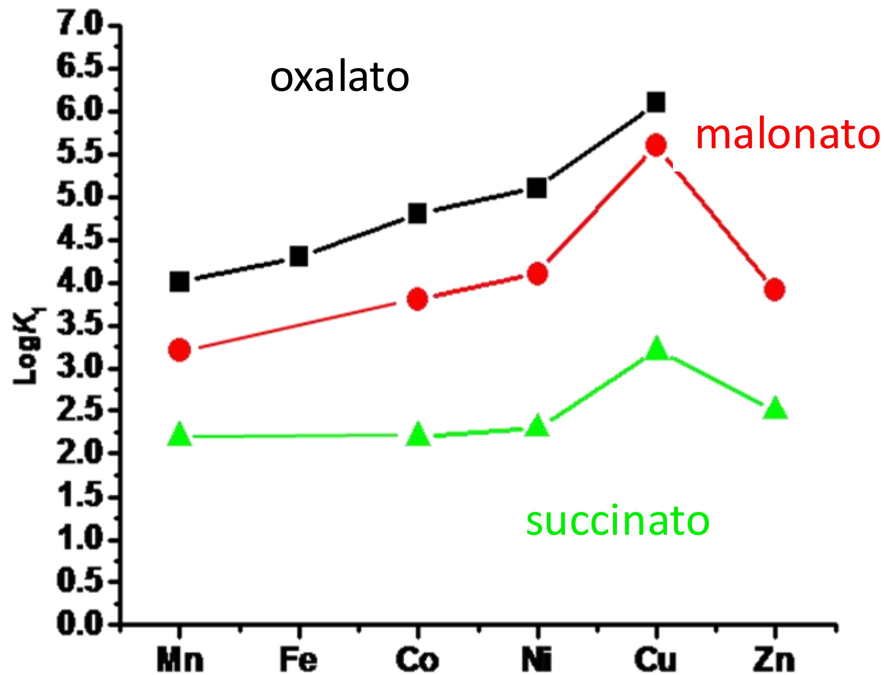


6-membered
malonato

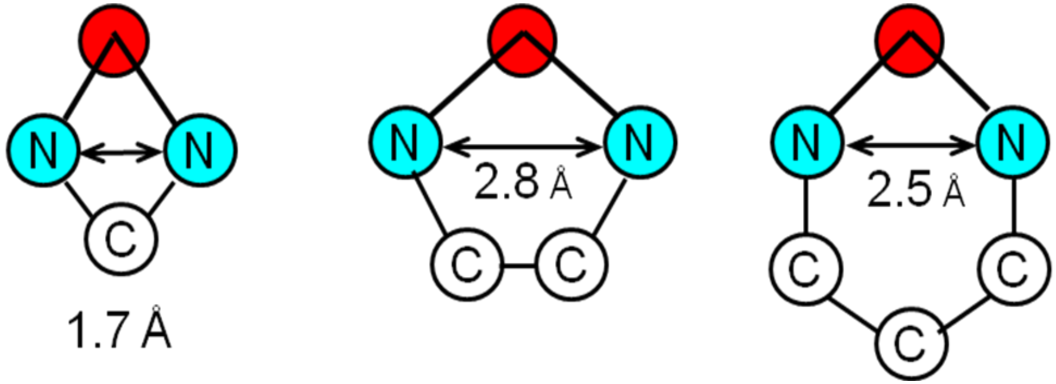


7-membered
succinato

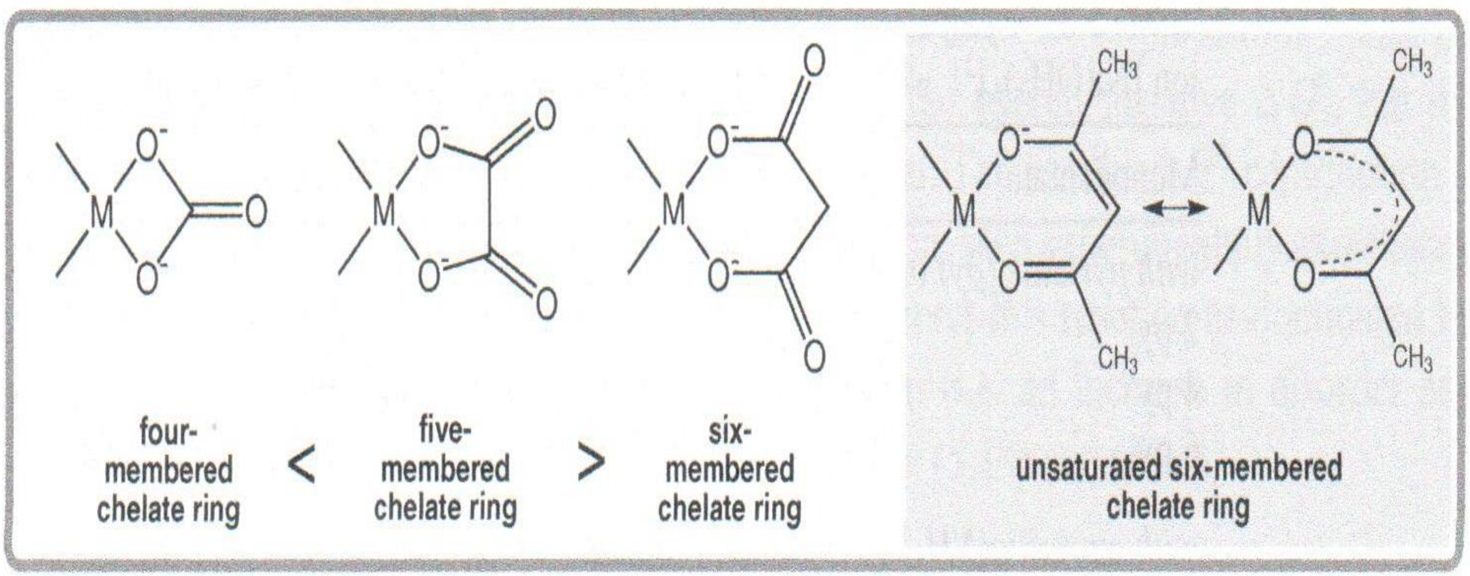




Improved stability in 5-membered rings: The chelate effect

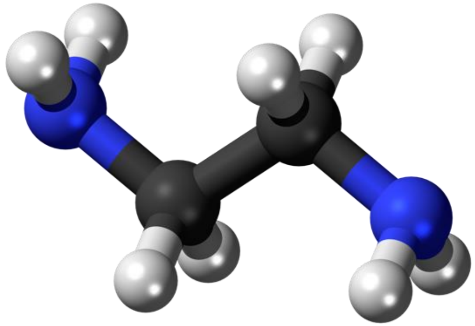


The exception – rings that contain unsaturated carbon atoms

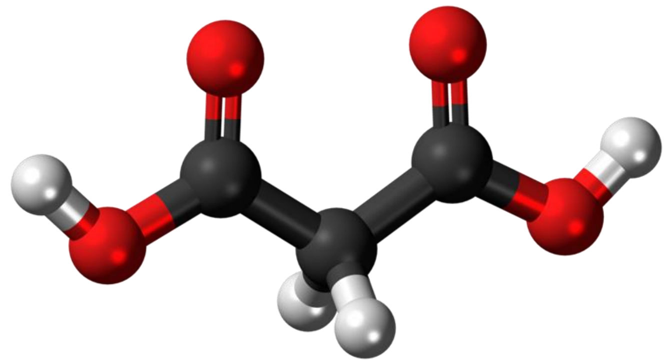


carbonato oxalato malanato acetylacetonato (acac)

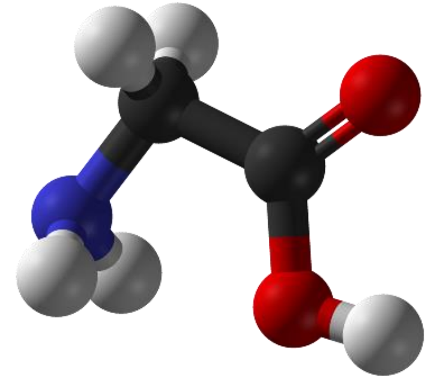
Predict the order of stabilities for the following with Ni^{2+}



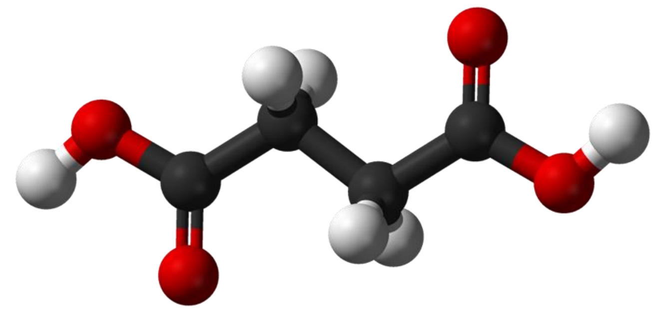
1). Ethylenediamine
NH_2-CH_2-CH_2-NH_2



2). Malonic acid
$^{-}O_2C$-CH_2-CO_2^{-}

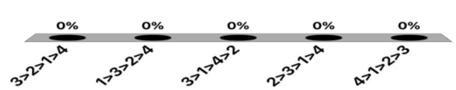


3). Glycine
NH_2-CH_2-CO_2^{-}

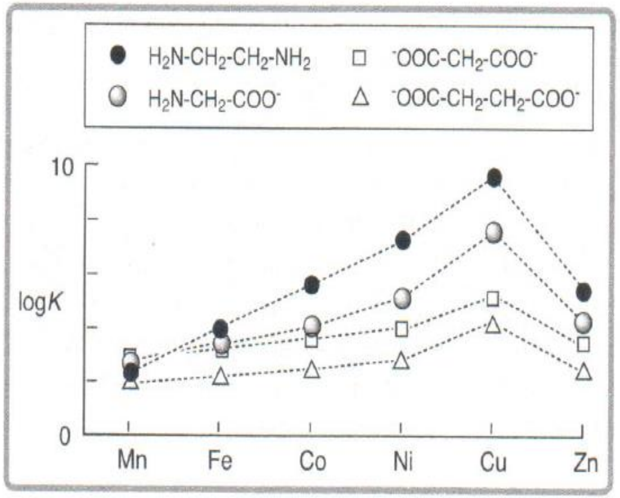


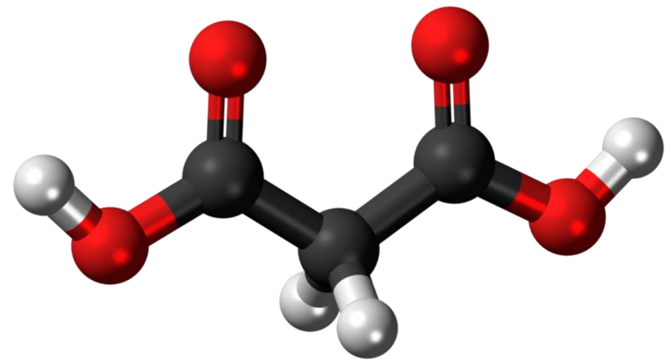
4). Succinic acid
$^{-}O_2C$-CH_2-CH_2-CO_2^{-}

A. 3>2>1>4
B. 1>3>2>4
C. 3>1>4>2
D. 2>3>1>4
E. 4>1>2>3

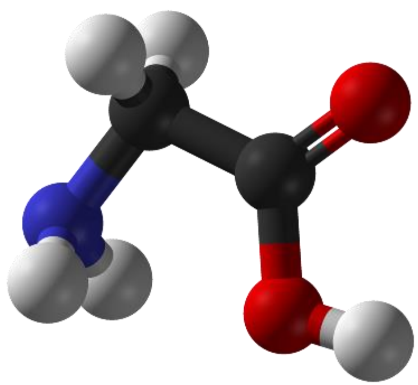


Exercise: Predict the order of stabilities for the following with Ni^{2+}

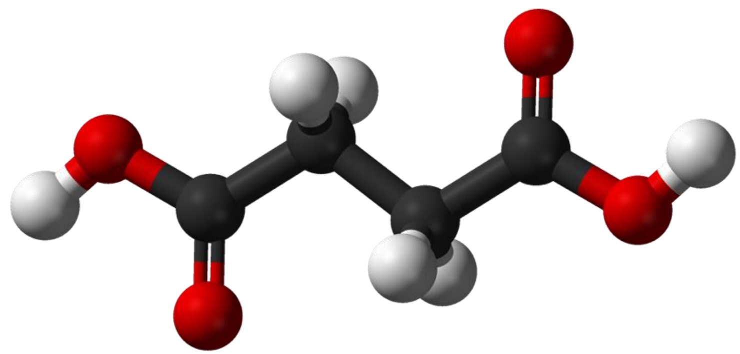




2). Malonic acid
$^{-}O_2C\text{-}CH_2\text{-}CO_2^{-}$



3). Glycine
$NH_2\text{-}CH_2\text{-}CO_2^{-}$



4). Succinic acid
$^{-}O_2C\text{-}CH_2\text{-}CH_2\text{-}CO_2^{-}$

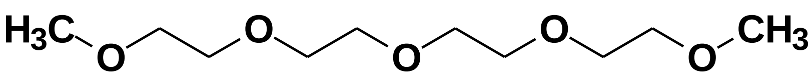
Answer: With Ni^{2+} being intermediate, it makes it difficult to apply HSAB. Considering Bronsted basicity and ring size we have the following stabilities 1>3>2>4

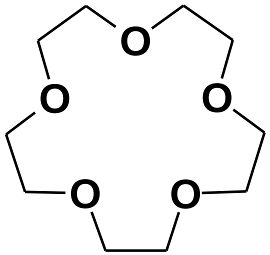
Macrocyclic effect

Which one of the below examples forms the most stable complex? Why?

Linear Tetraglyme or the 15-crown-5 analog….

$H_3C{-}O{-}(CH_2{-}CH_2{-}O)_4{-}CH_3$ **15P5**





$La^{3+}(solv) + 15P5 \rightleftharpoons [La(15P5)]^{3+} + 5\ solv$

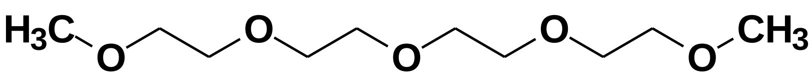
$La^{3+}(solv) + 15C5 \rightleftharpoons [La(15C5)]^{3+} + 5\ solv$

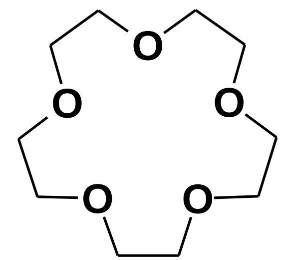
Macrocyclic effect

Which one of the below examples forms the most stable complex? Why?

Linear Tetraglyme or the 15-crown-5 analog....

$H_3C{-}O{-}(CH_2{-}CH_2{-}O)_4{-}CH_3$ **15P5**





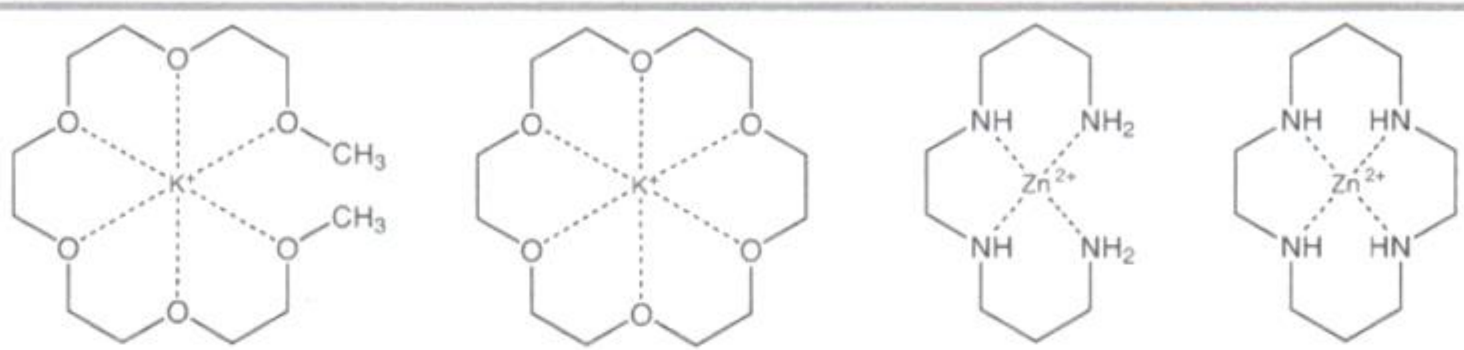
$La^{3+}(solv) + 15P5 \rightleftharpoons [La(15P5)]^{3+} + 5\ solv$

$\log K_f = 5.04$

$La^{3+}(solv) + 15C5 \rightleftharpoons [La(15C5)]^{3+} + 5\ solv$

$\log K_f = 6.48$

Some other common examples....



$\log K = 2.1$ **linear** pentaglyme

$\log K = 6.1$ **macrocyclic** 18-crown-6

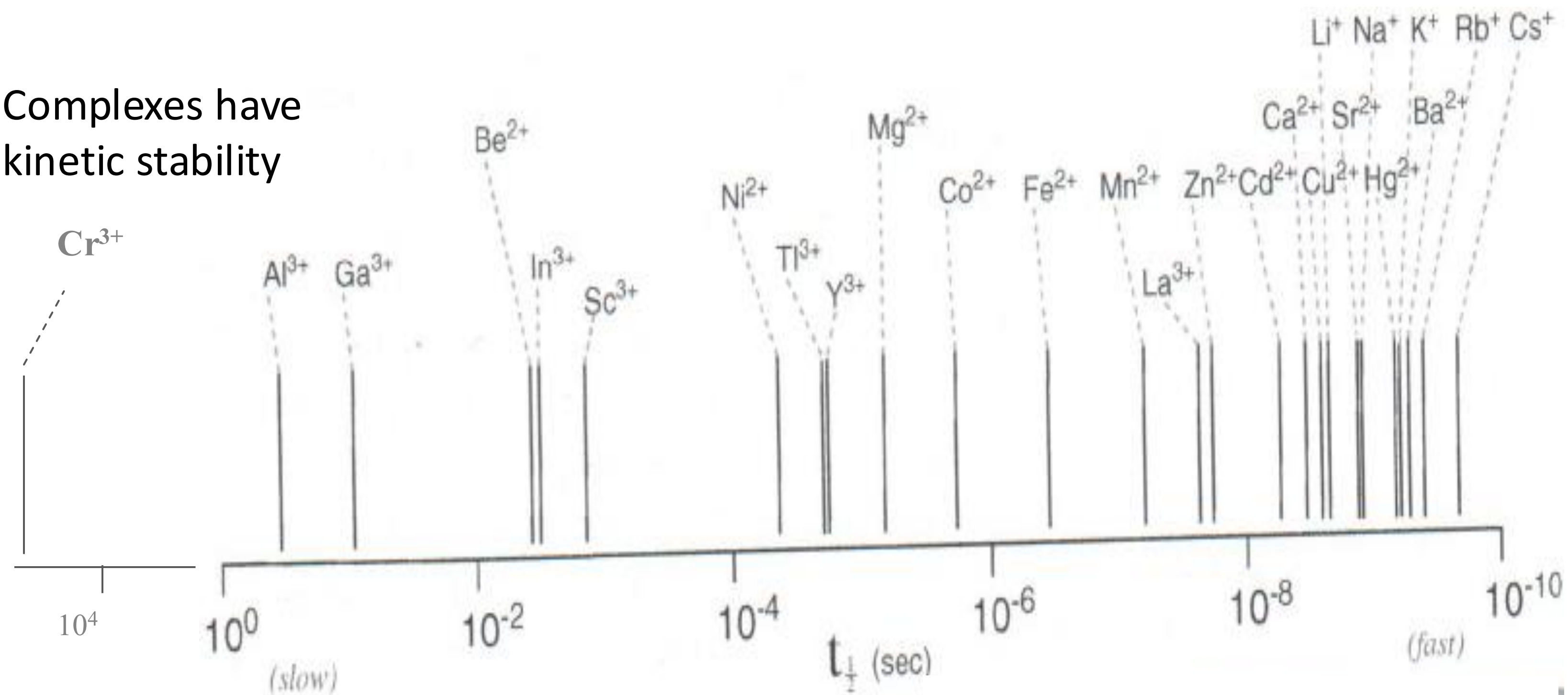
$\log K = 11.2$ **linear** 3,2,3-tet

$\log K = 15.3$ **macrocyclic** cyclam

Kinetics – How do we get to equilibrium?

Influenced by charge, radius, and electronic configuration

Complexes have kinetic stability



General Trends:

Labile, metal complexes that have electrons in the eg* orbitals. Some examples include high spin Co^{2+} (t_{2g}^5 e_g^2) and high spin Fe^{2+} (t_{2g}^4 e_g^2) and all complexes with less than 3 electrons.

Inert, octahedral d^3 complexes such as Cr^{3+} (t_{2g}^3 e_g^0) and low-spin d^4, d^5, and d^6 complexes.