

## THE PERIODIC TABLE

**SYMBOL**  
1 ATOMIC NUMBER  
2 ATOMIC WEIGHT  
3 NAME

( ) = ESTIMATES

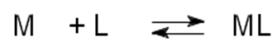
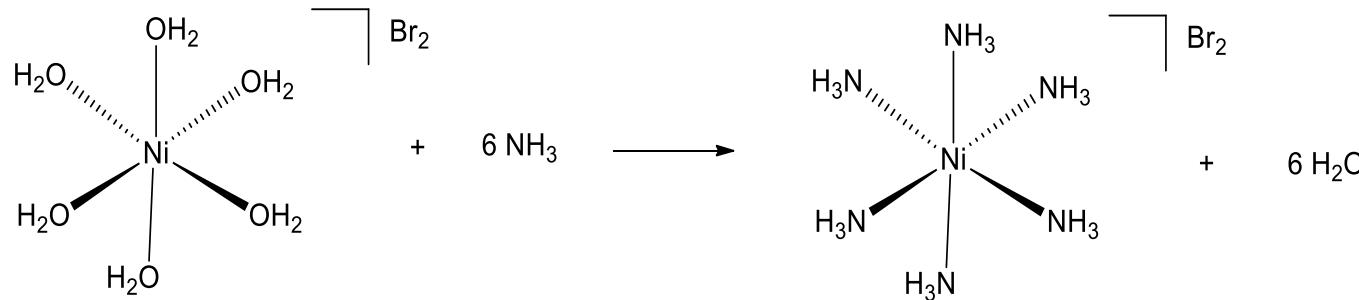
1 IA		18 VIIIA															
H	He	2 IIA		3 IIIA		4 IVA		5 VA		6 VIA							
<b>Li</b> 3 6.94 Lithium	<b>Be</b> 4 9.01 Boron	<b>H</b> 1 1.008 Hydrogen		<b>Na</b> 11 22.99 Sodium	<b>Mg</b> 12 24.31 Magnesium	<b>Al</b> 13 26.98 Aluminum	<b>Si</b> 14 28.09 Silicon	<b>P</b> 15 30.97 Phosphorus	<b>S</b> 16 32.07 Sulfur	<b>Cl</b> 17 35.45 Chlorine	<b>Ne</b> 18 20.18 Neon						
<b>K</b> 19 39.12 Potassium	<b>Ca</b> 20 40.08 Calcium	<b>Sc</b> 21 44.96 Scandium	<b>Ti</b> 22 47.88 Titanium	<b>V</b> 23 50.94 Vanadium	<b>Cr</b> 24 52.00 Chromium	<b>Mn</b> 25 54.94 Manganese	<b>Fe</b> 26 55.85 Iron	<b>Co</b> 27 58.93 Cobalt	<b>Ni</b> 28 58.69 Nickel	<b>Cu</b> 29 63.55 Copper	<b>Zn</b> 30 65.39 Zinc	<b>Ga</b> 31 69.72 Gallium	<b>Ge</b> 32 72.61 Germanium	<b>As</b> 33 74.92 Arsenic	<b>Se</b> 34 78.95 Selenium	<b>Br</b> 35 79.90 Bromine	<b>Kr</b> 36 83.80 Krypton
<b>Rb</b> 37 85.47 Rubidium	<b>Sr</b> 38 87.62 Strontium	<b>Y</b> 39 88.91 Yttrium	<b>Zr</b> 40 91.23 Zirconium	<b>Nb</b> 41 92.93 Niobium	<b>Mo</b> 42 95.94 Molybdenum	<b>Tc</b> 43 (97.9) Technetium	<b>Ru</b> 44 101.07 Ruthenium	<b>Rh</b> 45 102.91 Rhodium	<b>Pd</b> 46 106.42 Palladium	<b>Ag</b> 47 107.87 Silver	<b>Cd</b> 48 112.41 Cadmium	<b>In</b> 49 114.82 Indium	<b>Sn</b> 50 118.71 Tin	<b>Sb</b> 51 121.79 Antimony	<b>Te</b> 52 127.58 Tellurium	<b>I</b> 53 136.90 Iodine	<b>Xe</b> 54 131.29 Xenon
<b>Cs</b> 55 132.91 Cesium	<b>Ba</b> 56 137.33 Barium	<b>La</b> 57 138.91 Lanthanum	<b>Hf</b> 72 178.48 Hafnium	<b>Ta</b> 73 180.96 Tantalum	<b>W</b> 74 183.85 Tungsten	<b>Re</b> 75 186.21 Rhenium	<b>Os</b> 76 190.2 Osmium	<b>Ir</b> 77 192.27 Iridium	<b>Pt</b> 78 195.08 Platinum	<b>Au</b> 79 196.97 Gold	<b>Hg</b> 80 200.53 Mercury	<b>Tl</b> 81 204.28 Thallium	<b>Pb</b> 82 207.2 Lead	<b>Bi</b> 83 208.58 Bismuth	<b>Po</b> 84 (209) Polonium	<b>At</b> 85 (223) Astatine	<b>Rn</b> 86 (222) Radium
<b>Fr</b> 87 223.02 Francium	<b>Ra</b> 88 226.03 Radium	<b>Ac</b> 89 227.03 Actinium	<b>Rf</b> 93 (261) Rutherfordium	<b>Db</b> 106 (265) Dubnium	<b>Sg</b> 106 (262) Sergoron	<b>Bh</b> 107 (263) Bohrium	<b>Hs</b> 108 (265) Hassium	<b>Mt</b> 109 (266) Moscovium	Ununennium 110 Ununtrium 111 Ununpentium 112 Ununhexium	Ununtrium 113 Ununhexium 114 Ununpentium	Ununpentium 115 Ununhexium 116 Ununhexium	Ununhexium 117 Ununpentium 118 Ununpentium	Ununpentium 119 Ununpentium 120 Ununpentium	Ununpentium 121 Ununpentium 122 Ununpentium	Ununpentium 123 Ununpentium 124 Ununpentium	Ununpentium 125 Ununpentium 126 Ununpentium	Ununpentium 127 Ununpentium 128 Ununpentium
HEAVY METALS		HEAVY METALS															

LANTHANIDES											
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
58 140.12 Cerium	59 140.91 Praseodymium	60 144.24 Neodymium	61 (145) Promethium	62 150.38 Samarium	63 152.87 Europium	64 158.28 Gadolinium	65 160.93 Terbium	66 162.93 Dysprosium	67 164.90 Holmium	68 167.28 Erbium	69 168.13 Thulium
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md
90 228.04 Thorium	91 231.04 Protactinium	92 233.03 Uranium	93 237.06 Neptunium	94 (240) Plutonium	95 243.06 Americium	96 (247) Curium	97 (249) Berkelium	98 (251) Californium	99 (253) Einsteinium	100 (254) Fermium	101 (257) Mendelevium
Yb	Lu										
71 174.97 Lutetium	72 175.04 Lanthanum										

# Week 6

# Review of Chapter 2

Ligand substitution reactions and formation constants

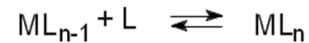


$$K_f^1 = \frac{[ML]}{[M] \cdot [L]}$$



$$K_f^2 = \frac{[ML_2]}{[ML] \cdot [L]}$$

.....



$$K_f^n = \frac{[ML_n]}{[ML_{n-1}] \cdot [L]}$$



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

$K_f$  tells us:

Which way the reaction proceeds

Which product is more stable

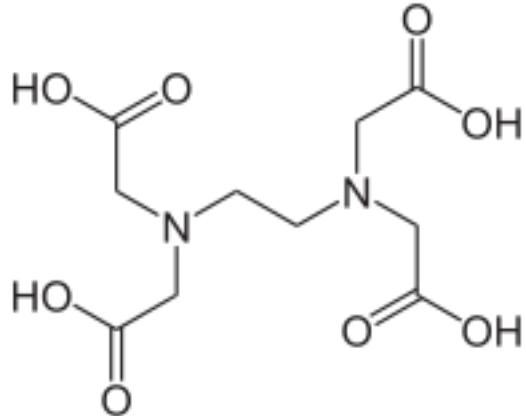
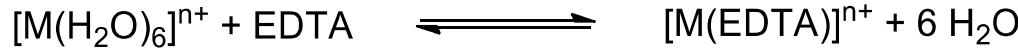
Formation constants of  $Ni^{2+}$  ammines,  $[Ni(NH_3)_n(OH_2)_{6-n}]^{2+}$

n	pK <sub>n</sub>	K <sub>n</sub>	K <sub>n</sub> /K <sub>n-1</sub>
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

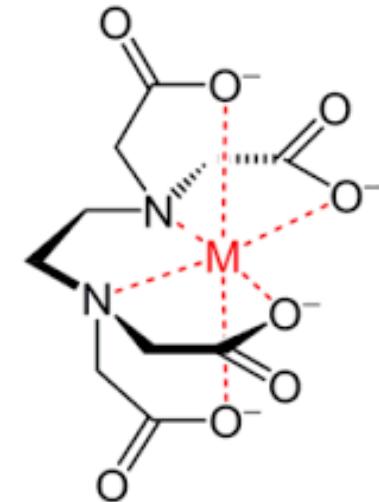
$$K_1 > K_2 > K_3 > K_4 > K_5 > K_6$$

$K_n$  is usually expressed as  $pK_n$

# Formation constants of $K_f^1$ for various metal-EDTA complexes



Metal ions	Log ( $K_f^1$ )
$\text{Ag}^+$	7.3
$\text{Ca}^{2+}$	10.8
$\text{Cu}^{2+}$	18.7
$\text{Ni}^{2+}$	18.6
$\text{Fe}^{2+}$	14.3
$\text{Fe}^{3+}$	25.1
$\text{Co}^{2+}$	16.1
$\text{Co}^{3+}$	36.0
$\text{V}^{2+}$	12.7
$\text{V}^{3+}$	25.9



## Take home messages:

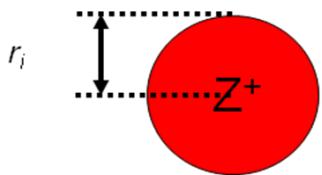
- Very large  $K_f$  value indicates reactants are used up
- EDTA complex is extremely stable relative to water complex
- Charge density of metal goes up so does  $K_f$
- Indicates relative differences in stability of complexes

$$\Delta G^\circ = -RT\ln K, R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{enthalpic stabilization or entropic stabilization}$$

# How to determine the relative differences in stability in complexes

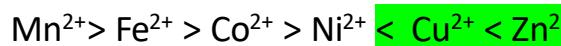
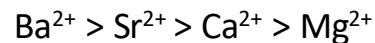
- 1) Charge and size of metals (charge density) – electrostatic interactions of spherical metals and ligands



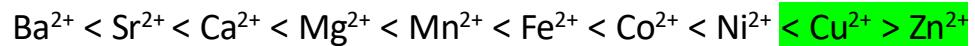
- higher the  $Z^2/r_i$  typically the larger the  $K_f$
- Applies to hard spherical ligands and metals

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

Ionic radii



According to Irving Williams Series



- 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
<i>Ligands</i>				
	$\text{F}^-$ , $\text{O}^{2-}$ , $\text{OH}$ , $\text{OH}_2$ , $\text{OHR}$ , $\text{RCOO}^-$ , $\text{NH}_3$ , $\text{NR}_3$ , $\text{RCN}$ , $\text{Cl}^-$ , $\text{NO}_3^-$ , $\text{CO}_3^{2-}$ , $\text{SO}_4^{2-}$ , $\text{PO}_4^{3-}$	$\text{Br}^-$ , $\text{SR}$ , $\text{NO}_2^-$ , $\text{N}_3^-$ , $\text{SCN}^-$ , $\text{H}_5\text{C}_5\text{N}$	$\text{PR}_3$ , $\text{SR}_2$ , $\text{SeR}_2$ , $\text{AsR}_3$ , $\text{CNR}$ , $\text{CN}^-$ , $\text{SCN}^-$ , $\text{CO}$ , $\text{I}^-$ , $\text{H}^-$ , $\text{R}^-$	
<i>Metal Ions</i>				
	$\text{Mo}^{5+}$ , $\text{Ti}^{4+}$ , $\text{V}^{4+}$ , $\text{Sc}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ , $\text{Co}^{3+}$ , $\text{Al}^{3+}$ , $\text{Eu}^{3+}$ , $\text{Cr}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Be}^{2+}$ , $\text{K}^+$ , $\text{Na}^+$ , $\text{Li}^+$ , $\text{H}^+$	$\text{Fe}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$	$\text{Cu}^+$ , $\text{Rh}^+$ , $\text{Ag}^+$ , $\text{Au}^+$ , $\text{Pd}^{2+}$ , $\text{Pt}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Cd}^{2+}$	

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	$\text{R}_3\text{N}$	$\text{R}_2\text{O}$	$\text{F}^-$	weakest
	$\text{R}_3\text{P}$	$\text{R}_2\text{S}$	$\text{Cl}^-$	
	$\text{R}_3\text{As}$	$\text{R}_2\text{Se}$	$\text{Br}^-$	
weakest	$\text{R}_3\text{Sb}$	$\text{R}_2\text{Te}$	$\text{I}^-$	strongest

## Trends:

- Hard metals:** high oxidation states  $> 2$  and early transition metals
- Soft metals:** late transition metals and low-oxidation states
- Intermediate metals:** first-row and  $2+$  oxidation state
- Hard ligands:** ligands with donors that are N, O, or halides.
- Soft ligands:** are carbon donors or elements found in the second or later rows of the p-block
- Polarizability and hence softness increases going down the periodic chart.

If a mixture of CO and NH<sub>3</sub> is added to a solution containing Fe(0), which ligand will preferentially bind to Fe?

- A. CO
- B. NH<sub>3</sub>

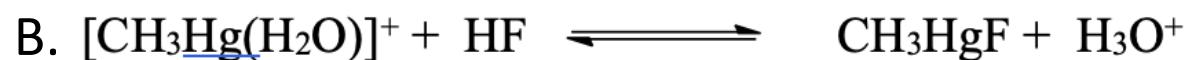
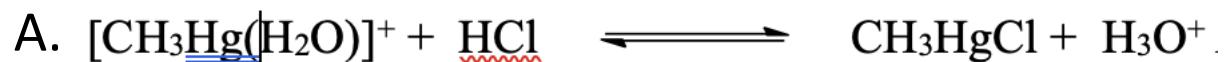


If a mixture of CO and NH<sub>3</sub> is added to a solution containing Fe(III), which ligand will preferentially bind to Fe?

- A. CO
- B. NH<sub>3</sub>



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



A. Reaction A

B. Reaction B

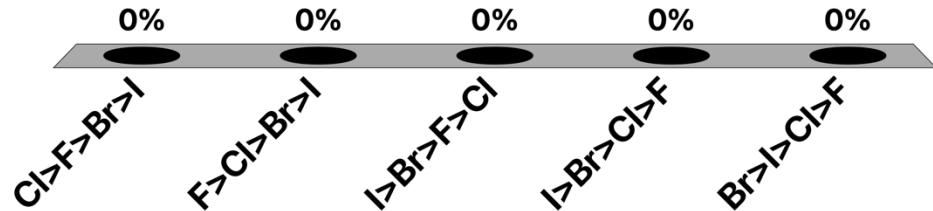


One reaction favors products and one reaction favors reactants. State which reaction favors products; explain your answer.



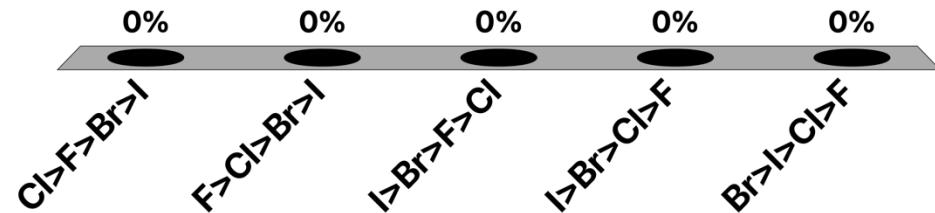
What do you expect the trend to look like for  $\text{Co}^{3+}$  and  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{F}^-$ . Please rank the complexes formed in the order of stability.

- A.  $\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$
- B.  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
- C.  $\text{I}^- > \text{Br}^- > \text{F}^- > \text{Cl}^-$
- D.  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
- E.  $\text{Br}^- > \text{I}^- > \text{Cl}^- > \text{F}^-$



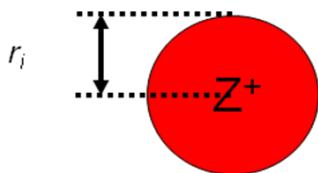
What do you expect the trend to look like for  $\text{Ag}^+$  and  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{F}^-$ . Please rank the complexes formed in the order of stability.

- A.  $\text{Cl}^- > \text{F}^- > \text{Br}^- > \text{I}^-$
- B.  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$
- C.  $\text{I}^- > \text{Br}^- > \text{F}^- > \text{Cl}^-$
- D.  $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$
- E.  $\text{Br}^- > \text{I}^- > \text{Cl}^- > \text{F}^-$



# How to determine the relative differences in stability in complexes

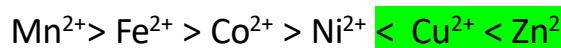
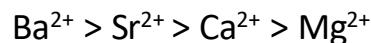
- 1) Charge and size of metals (charge density) – electrostatic interactions of spherical metals and ligands



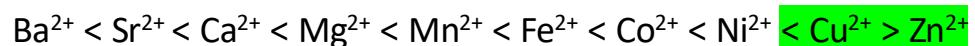
- higher the  $Z^2/r_i$  typically the larger the  $K_f$
- Applies to hard spherical ligands and metals

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

Ionic radii



According to Irving Williams Series



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

- 4) Strength of ligand as a **Bronsted base** - accepts  $\text{H}^+$  -

- 5) Structural Aspects of ligands

- Chelate effects
- Size of chelate rings
- Steric effects of ligands
- Macrocyclic effect

# How Bronsted basicity influences the stability of complexes

The stronger the **Bronsted Basicity** (ability to accept a  $\text{H}^+$  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.  $\text{Ag}^+$ , as indicated by the log of the  $K_f$  in ( ).

Stability of  $\text{Ag}^+$  complex  $\text{F}^-$  (0.3) <  $\text{Cl}^-$  (3.3) <  $\text{Br}^-$  (4.5) <  $\text{I}^-$  (8.0)

Acid strength  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$   
 $\text{PK}_a \text{ HF} > \text{HCl} > \text{HBr} > \text{HI}$

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

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

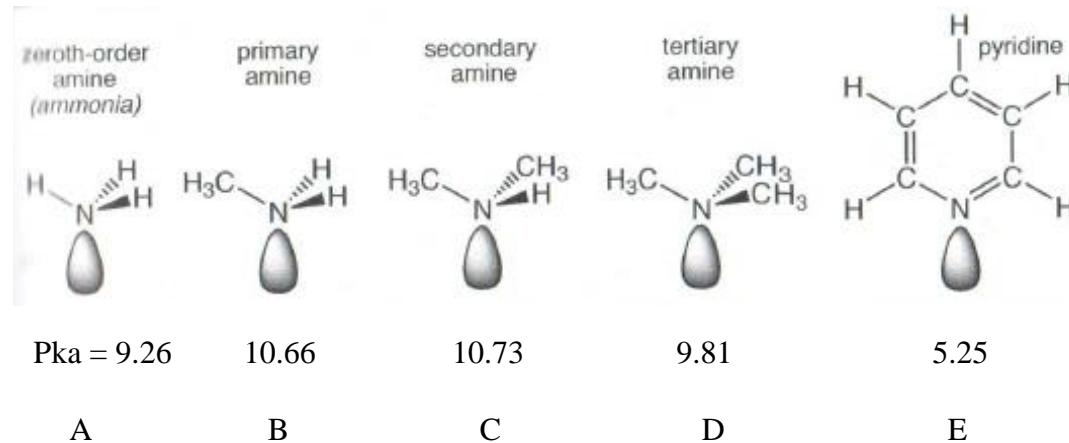
## Acid dissociation constant

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

as such the lower the  $\text{pK}_a$ , the stronger the acid and hence the weaker the conjugate base.

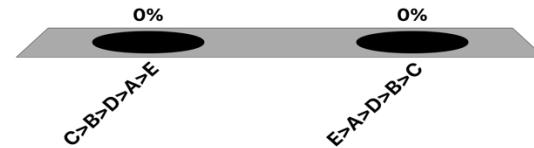
**Rule:** Ligands with higher  $\text{PK}_a$ 's tend to form stronger complexes with hard metals.

From the  $\text{PK}_a$ s of the conjugate acids, rank the following ligands in terms of their acid strength!

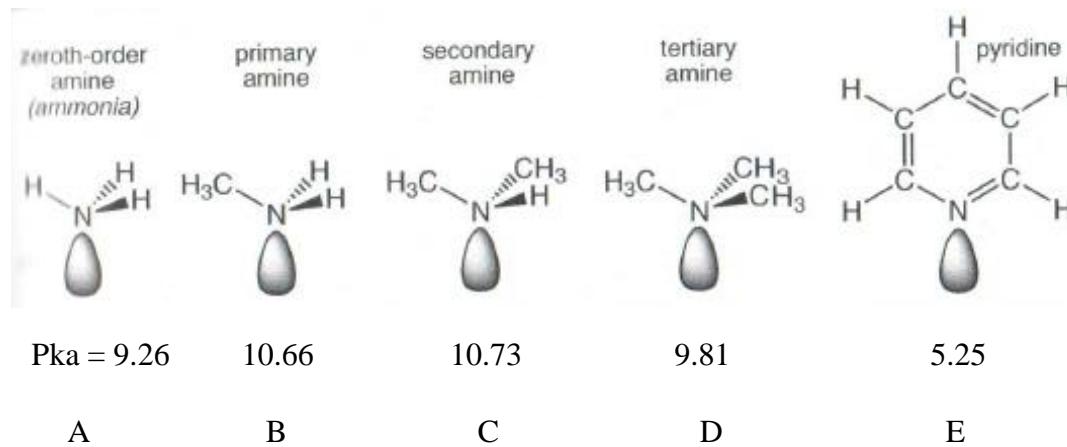


A. C>B>D>A>E

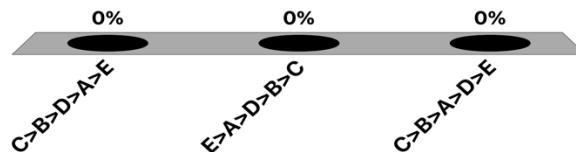
B. E>A>D>B>C



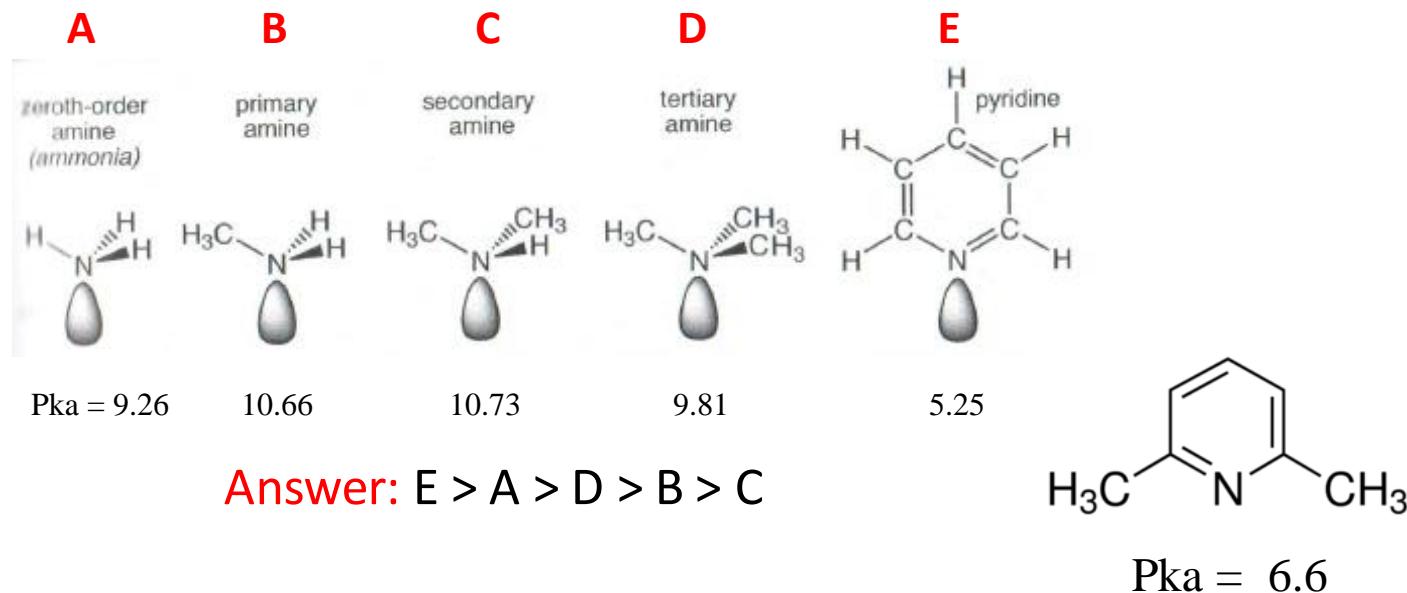
Based on what we just learned, which ligands do you think will form the strongest complex with  $\text{Co}^{3+}$ ? Please rank them.



- A. C>B>D>A>E
- B. E>A>D>B>C
- C. C>B>A>D>E



**Exercise:** From the Pk<sub>a</sub>s of the conjugate acids, rank the following ligands in terms of their acid strength!



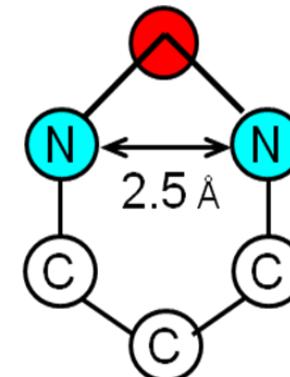
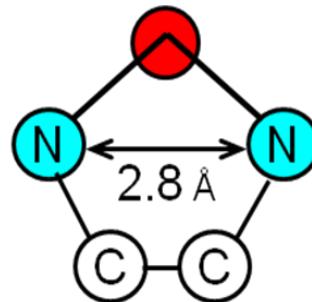
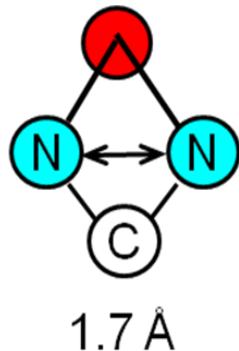
**Exercise:** Based on what we just learned, which ligand do you think will form the strongest complex with Co<sup>3+</sup>? Rank them.

**Answer:** C > B > A > D > E

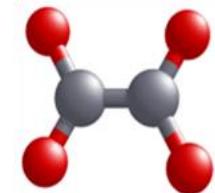
**Exercise:** Can anyone guess why this is the trend for the acidity with regard to the ammonia and the primary, secondary, and tertiary amines?

**Answer:** Sterically bulky ligands can counteract bases strength. This is reflected in the decrease in the Pk<sub>a</sub> for the tertiary amine, which leads to a less stable complex.

# Improved stability in 5-membered rings: The chelate effect



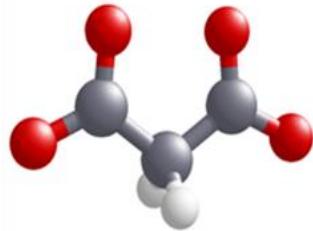
5-membered  
oxalato



2-

oxalato

6-membered  
malonato



2-

7-membered  
succinato



Log K<sub>stability</sub>

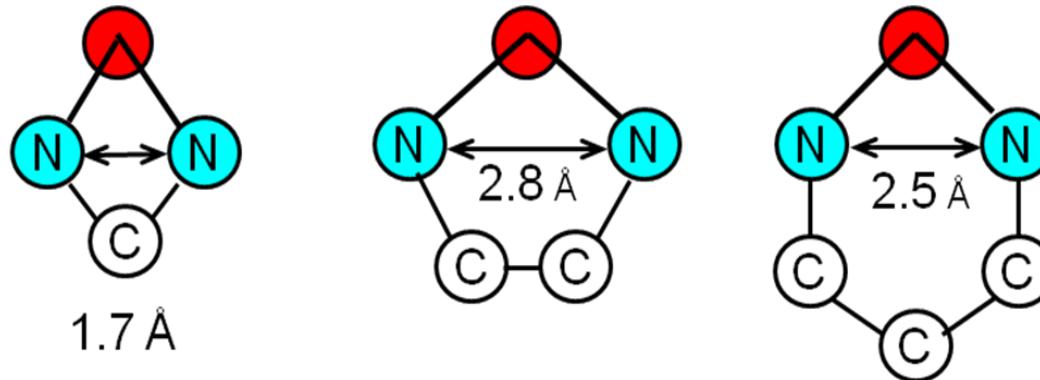
Mn Fe Co Ni Cu Zn

oxalato

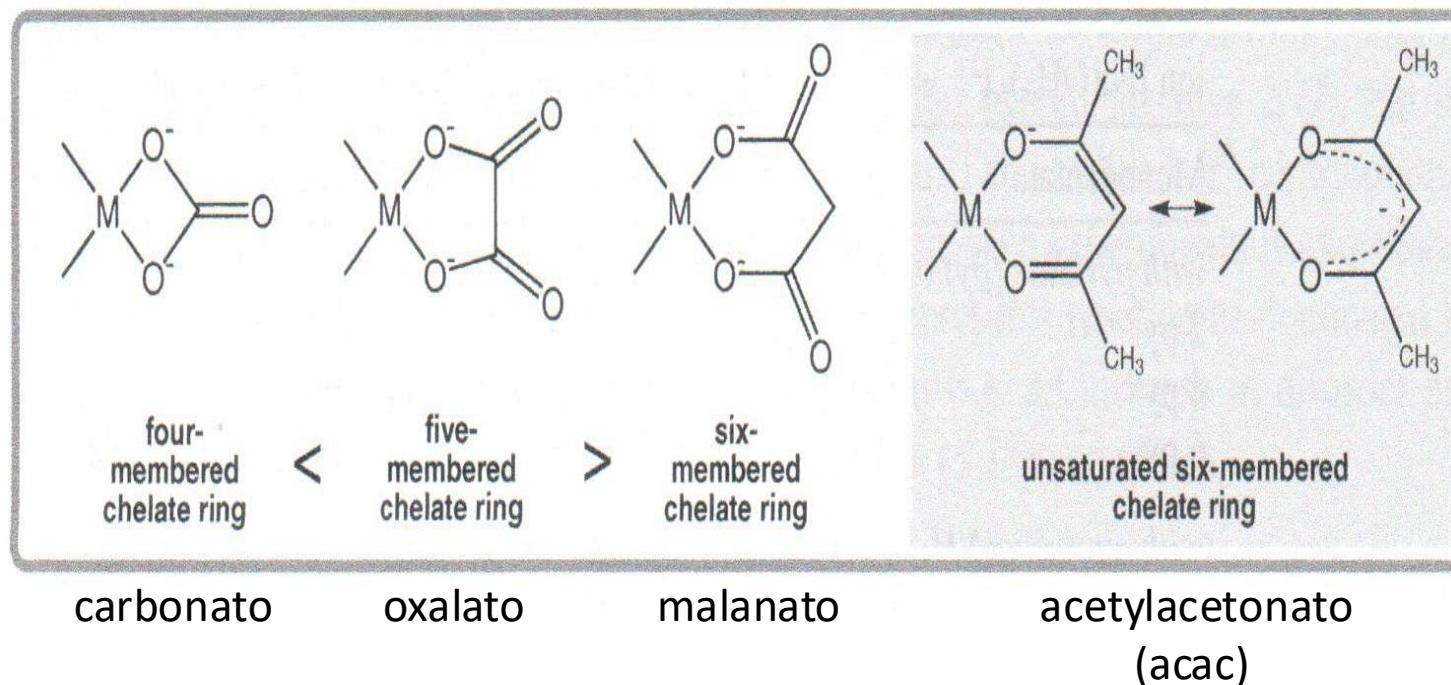
malonato

succinato

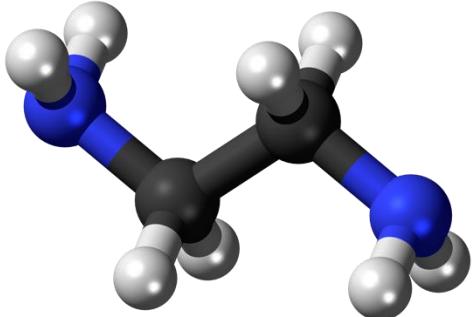
# Improved stability in 5-membered rings: The chelate effect



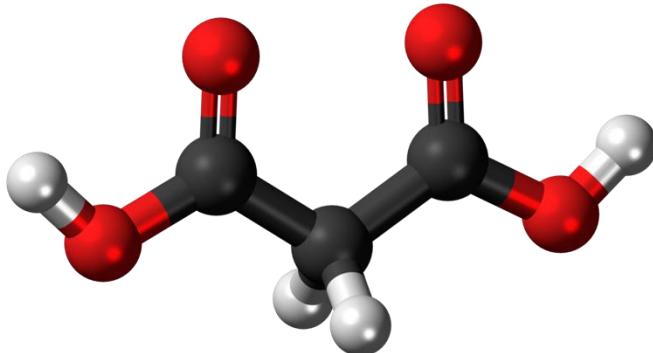
The exception – rings that contain unsaturated carbon atoms



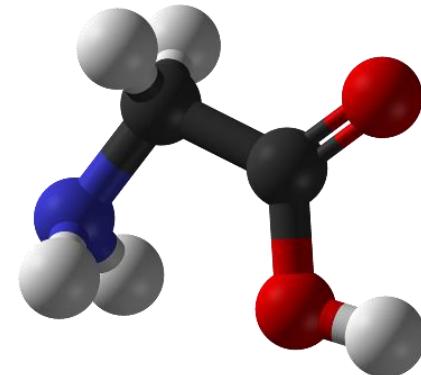
## Predict the order of stabilities for the following with $\text{Ni}^{2+}$



1). Ethylenediamine  
 $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$

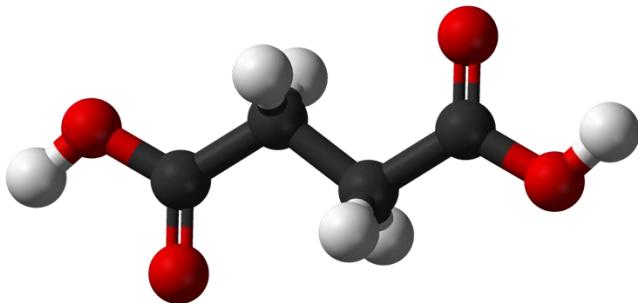


2). Malonic acid  
 $-\text{O}_2\text{C-CH}_2\text{-CO}_2^-$

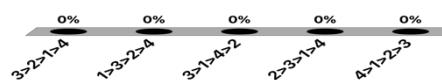


3). Glycine  
 $\text{NH}_2\text{-CH}_2\text{-CO}_2^-$

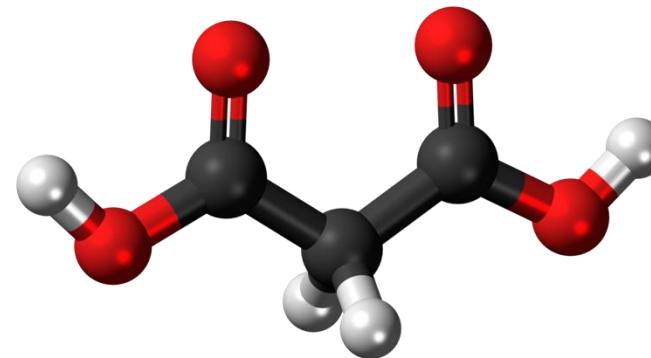
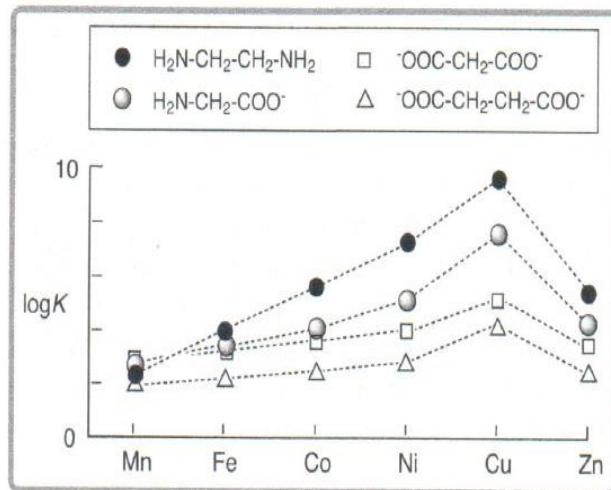
- A.  $3>2>1>4$
- B.  $1>3>2>4$
- C.  $3>1>4>2$
- D.  $2>3>1>4$
- E.  $4>1>2>3$



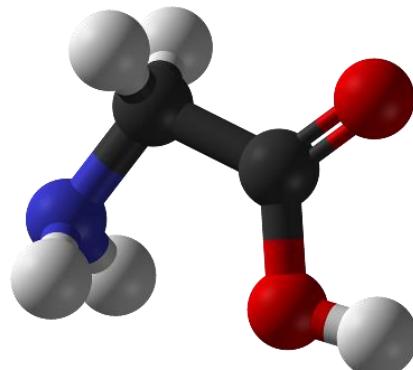
4). Succinic acid  
 $-\text{O}_2\text{C-CH}_2\text{-CH}_2\text{-CO}_2^-$



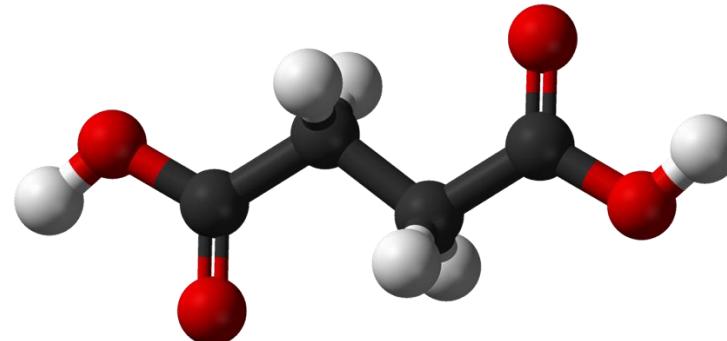
## Exercise: Predict the order of stabilities for the following with $\text{Ni}^{2+}$



2). Malonic acid  
 $-\text{O}_2\text{C}-\text{CH}_2-\text{CO}_2^-$



3). Glycine  
 $\text{NH}_2-\text{CH}_2-\text{CO}_2^-$



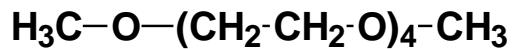
4). Succinic acid  
 $-\text{O}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CO}_2^-$

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

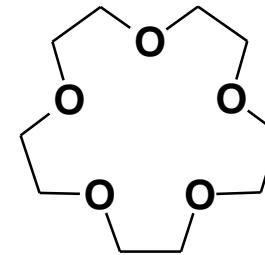
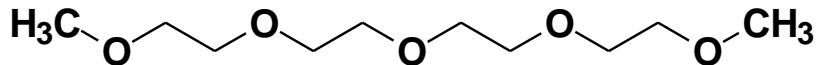
# Macrocyclic effect

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

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



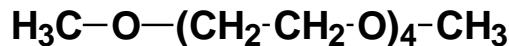
15P5



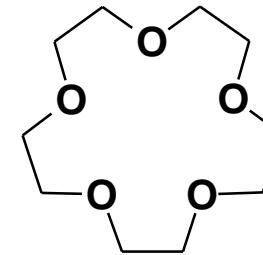
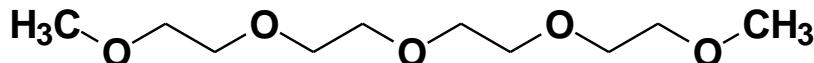
# Macrocyclic effect

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

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15P5

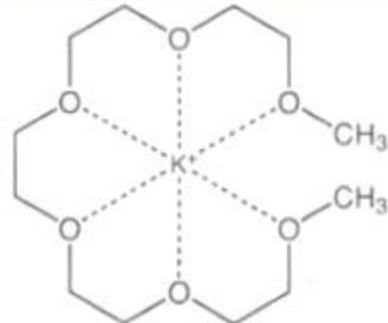


$$\text{Log } K_f = 5.04$$



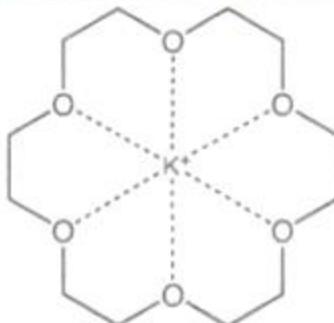
$$\text{Log } K_f = 6.48$$

Some other common examples....



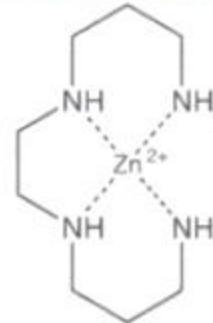
$$\log K = 2.1$$

linear pentaglyme



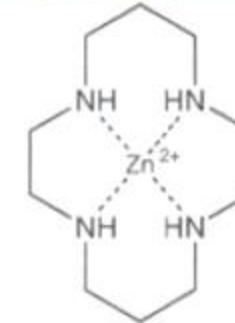
$$\log K = 6.1$$

macrocyclic 18-crown-6



$$\log K = 11.2$$

linear 3,2,3-tet



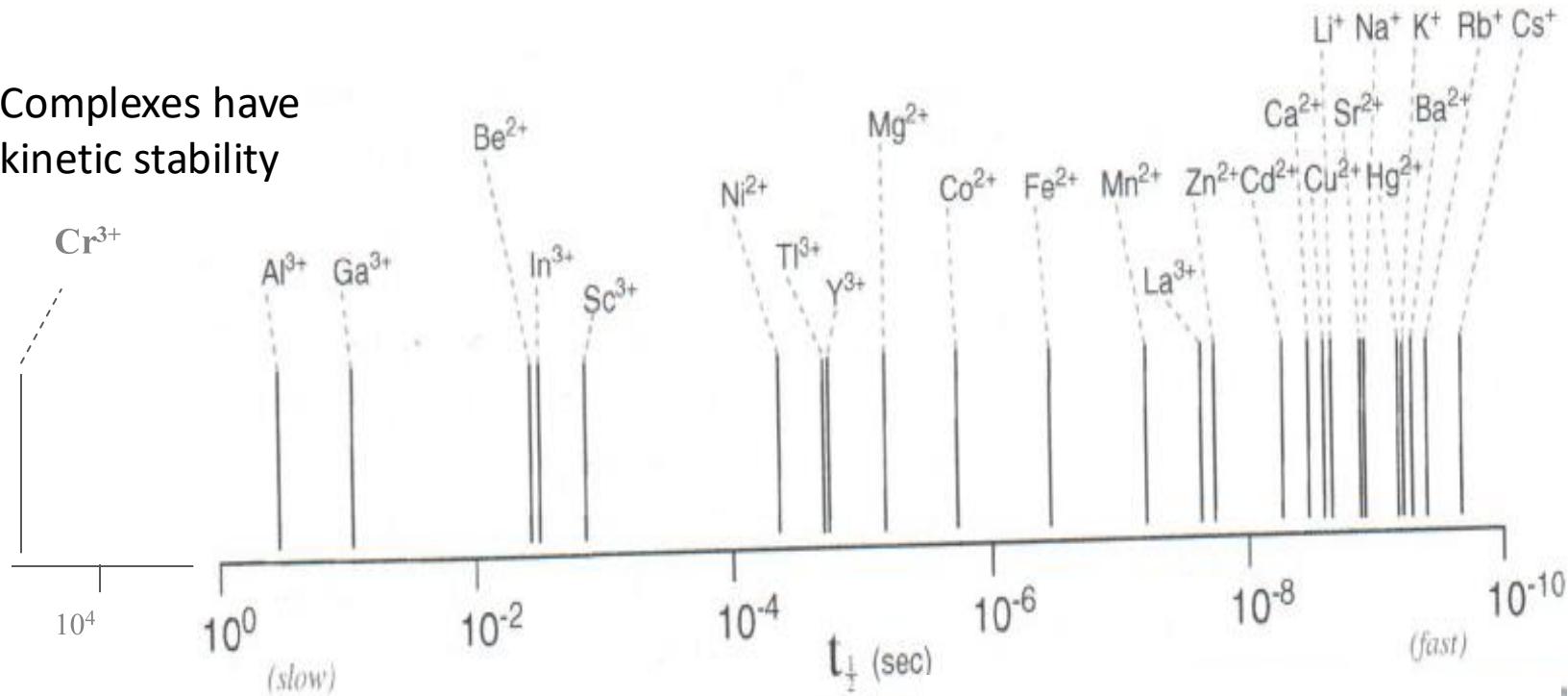
$$\log K = 15.3$$

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  $\text{eg}^*$  orbitals. Some examples include high spin  $\text{Co}^{2+}$  ( $t_{2g}^5 e_g^2$ ) and high spin  $\text{Fe}^{2+}$  ( $t_{2g}^4 e_g^2$ ) and all complexes with less than 3 electrons.

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