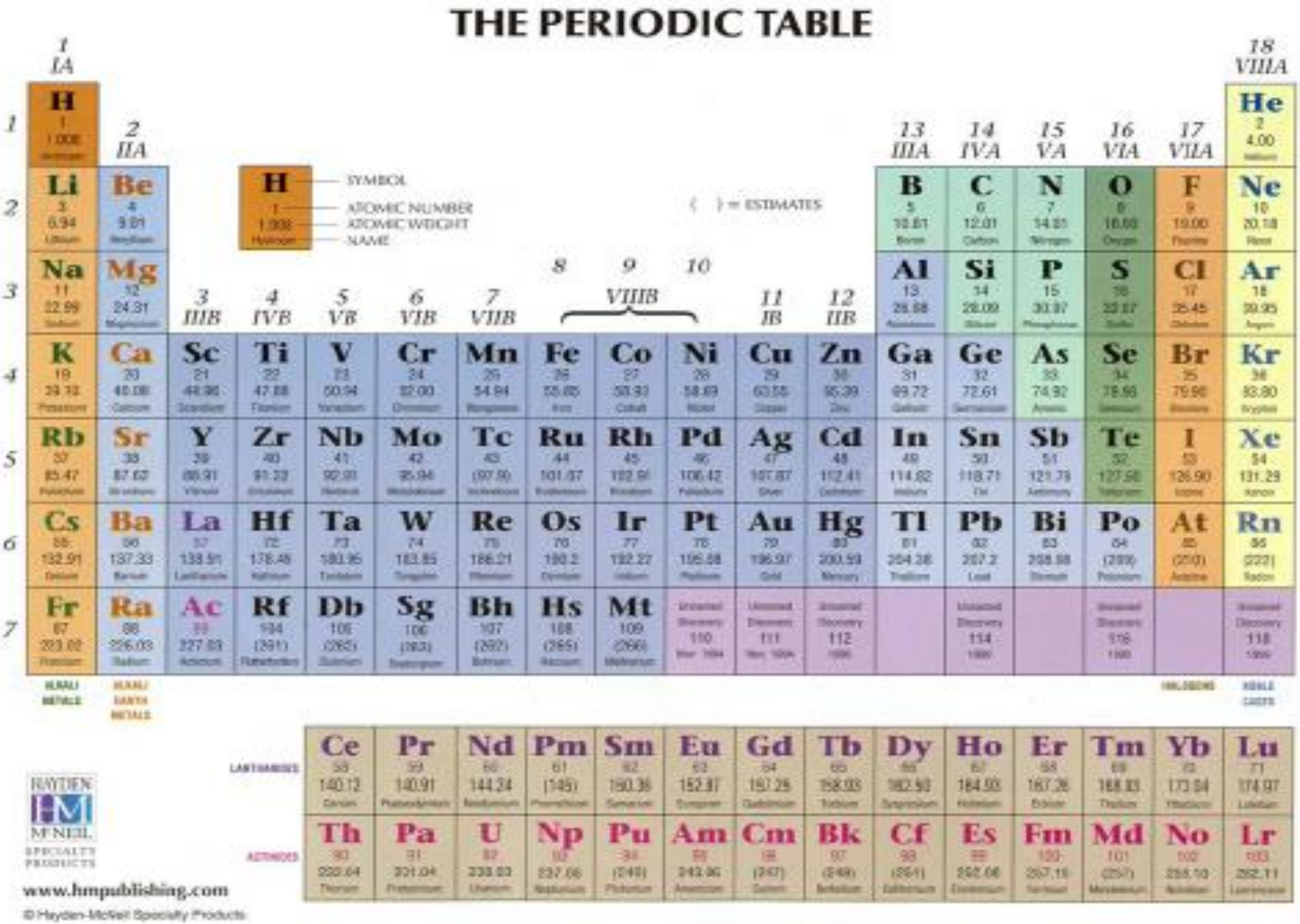
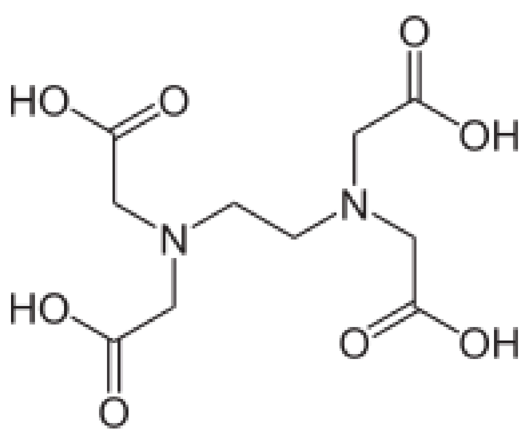

THE PERIODIC TABLE
1 IA
2 IIA
3 IIIB
4 IVB
5 VB
6 VIB
7 VIIB
8 9 10 VIIIB
11 IB
12 IIB
13 IIIA
14 IVA
15 VA
16 VIA
17 VIIA
18 VIIIA
SYMBOL
ATOMIC NUMBER
ATOMIC WEIGHT
NAME
( ) = ESTIMATES
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo 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

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

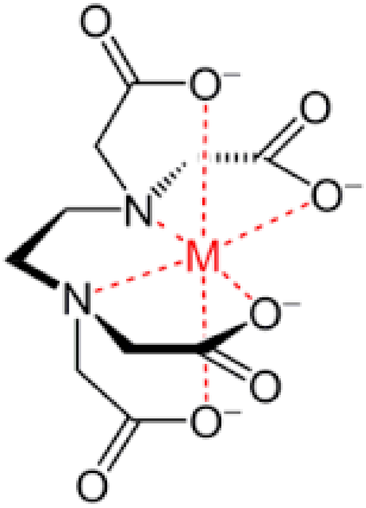
n	pK_n	K_n	K_n/K_{n-1}
1	-2.72	524.8	
2	-2.17	147.9	0.28
3	-1.66	45.71	0.53
4	-1.12	13.18	0.56
5	-0.67	4.677	0.53
6	-0.03	1.07	0.42

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

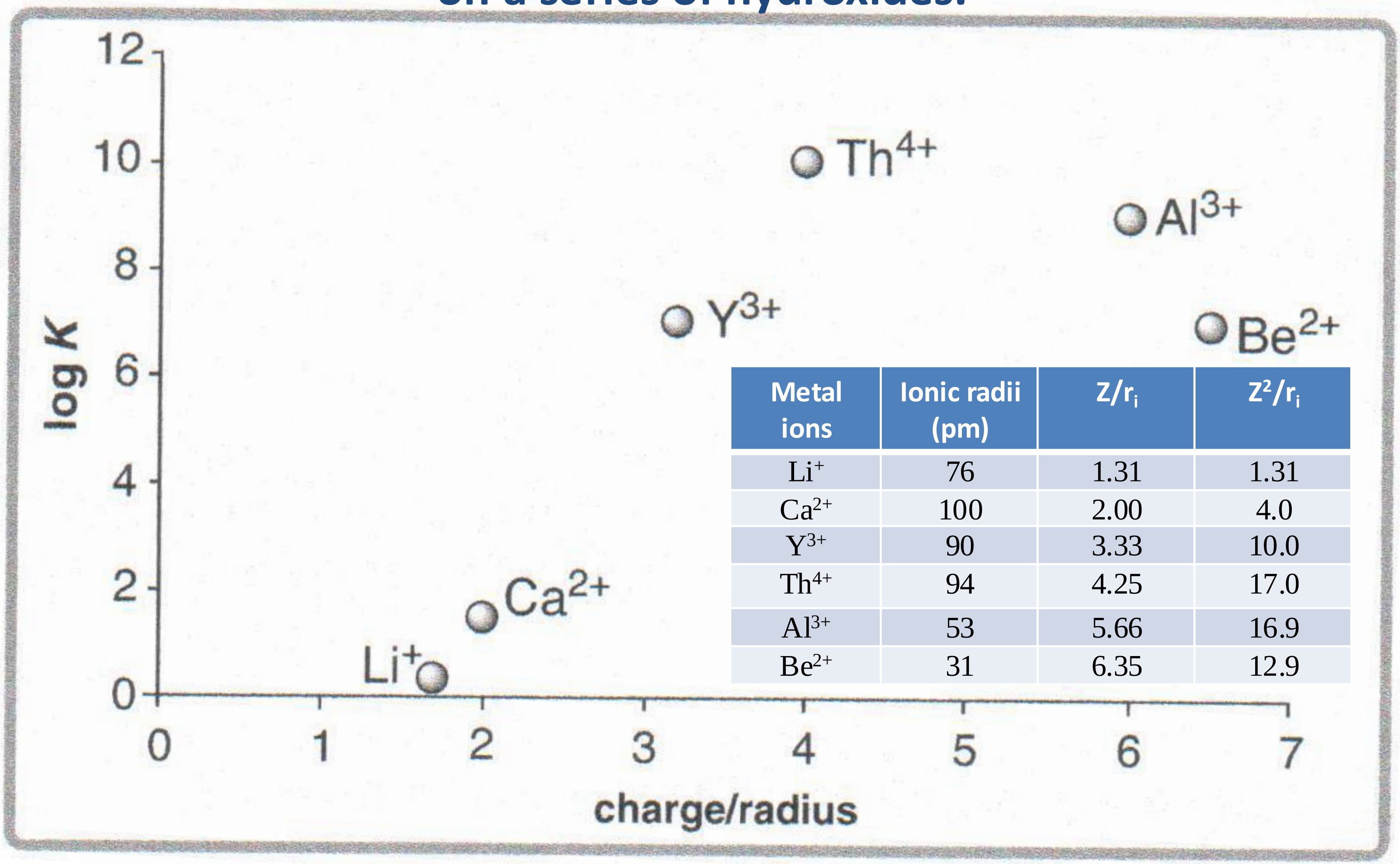
$$[M(H_2O)_6]^{n+} + EDTA \rightleftharpoons [M(EDTA)]^{n+} + 6\ H_2O$$



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

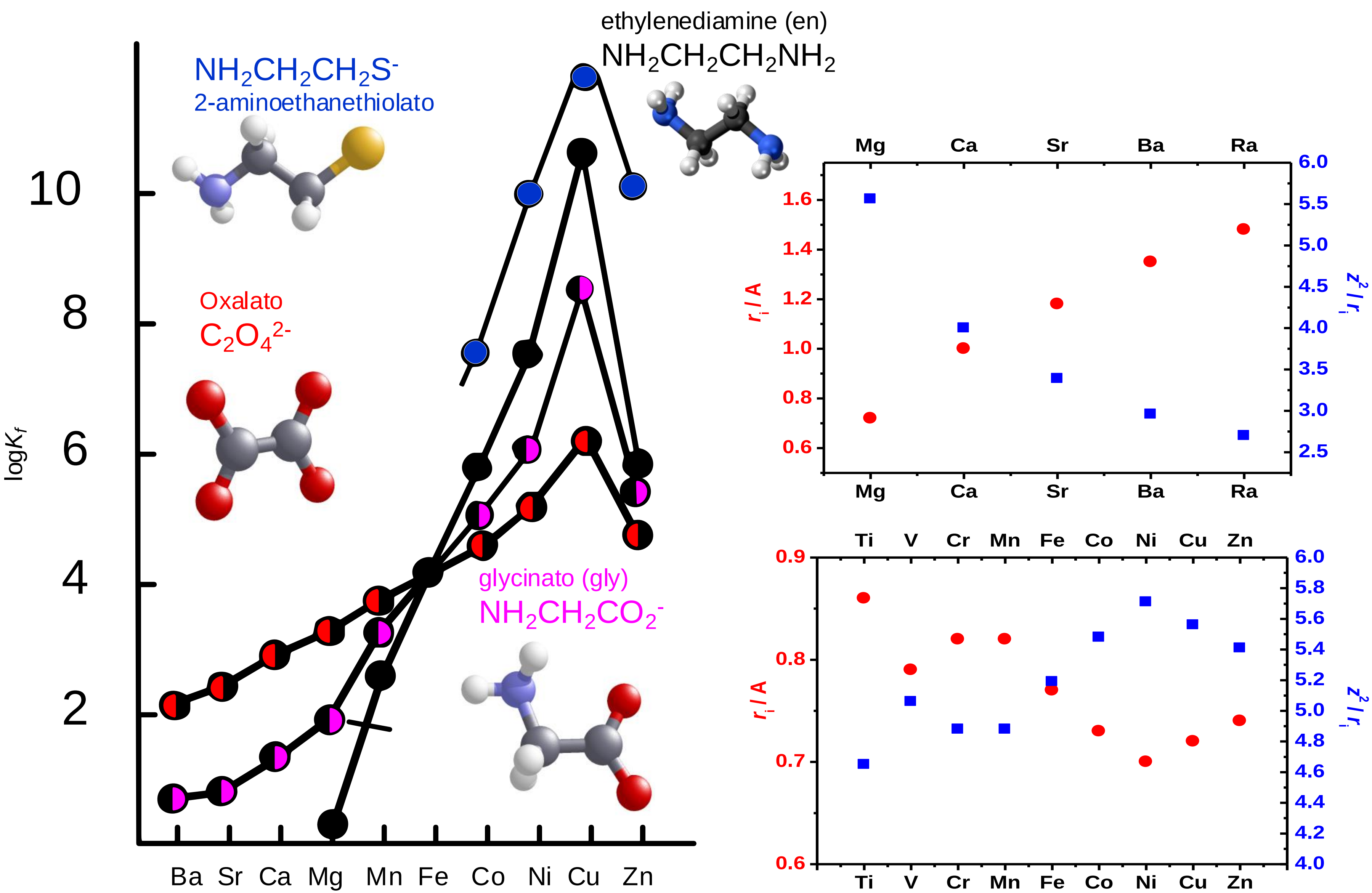


Influence of the charge and ionic radii of metal on stability on a series of hydroxides.



Metal ions	Ionic radii (pm)	Z/r_i	Z^2/r_i
Li^{+}	76	1.31	1.31
Ca^{2+}	100	2.00	4.0
Y^{3+}	90	3.33	10.0
Th^{4+}	94	4.25	17.0
Al^{3+}	53	5.66	16.9
Be^{2+}	31	6.35	12.9

Irving-William Series: stability of M^{2+} octahedral complexes with the different ligands follow the same trend, can it be explained with Z^2/r_i?



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

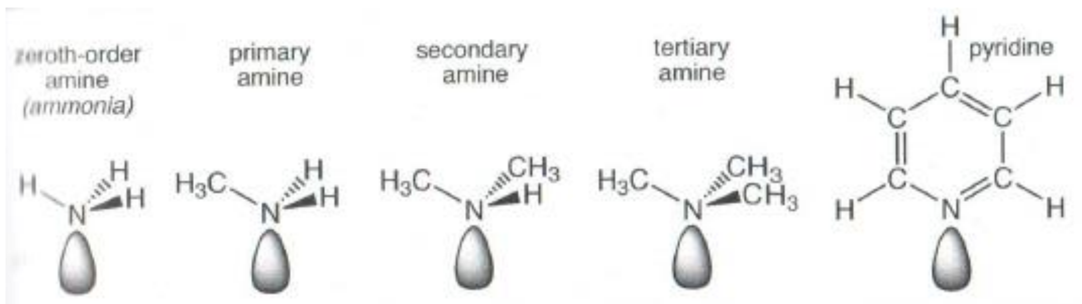
d. **Hard ligands:** ligands with donors that are N, O, or halides.

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.

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

A B C D E

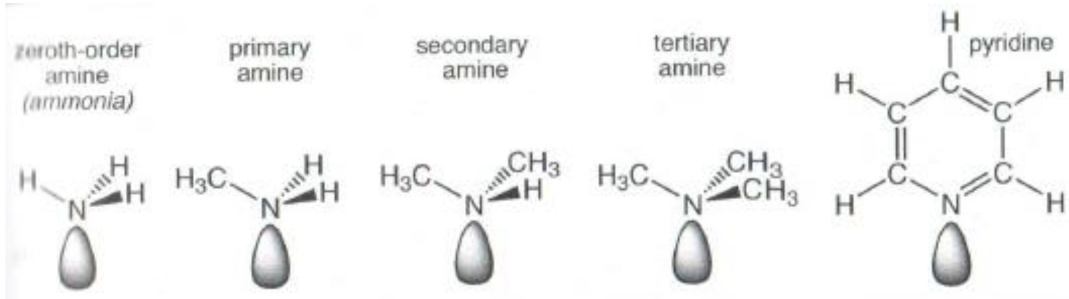


PK_a = 9.26	10.66	10.73	9.81	5.25

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

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

A B C D E



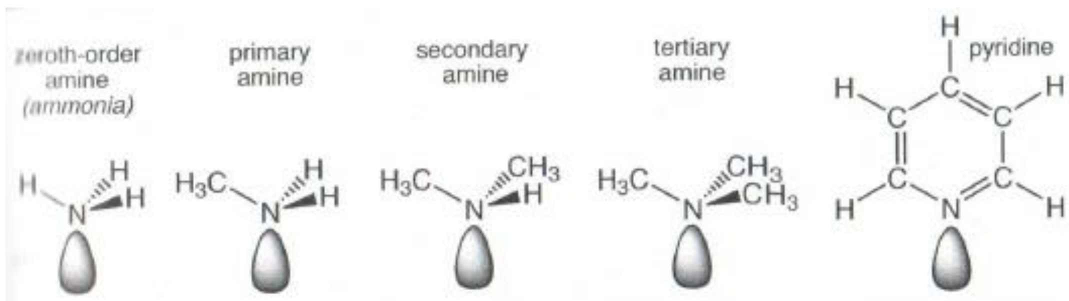
PK_a = 9.26 10.66 10.73 9.81 5.25

Answer: E > A > D > B > C

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

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

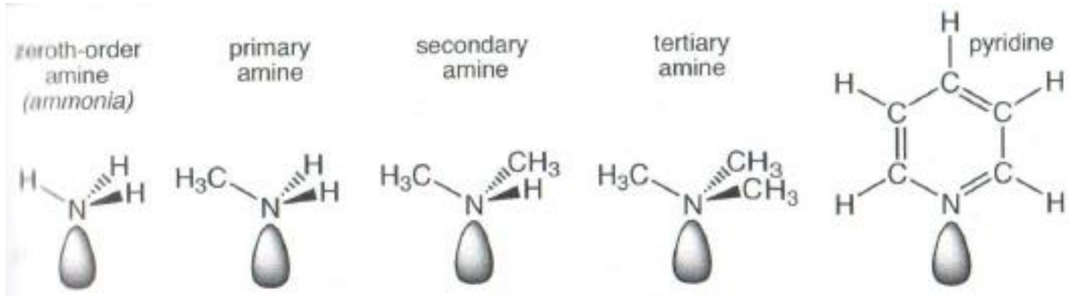
Exercise: Based on what we just learned, which ligand do you think will form the strongest complex with Co^{3+}? Rank them.

Answer: C > B > A > D > E

Exercise: Can anyone guess why D is more basic than A, but forms a weaker CO^{3+} complex than A?

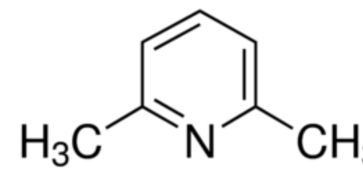
Exercise: From the Pkas of the congugate acids, rank the following ligands in terms of their acid strength!

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

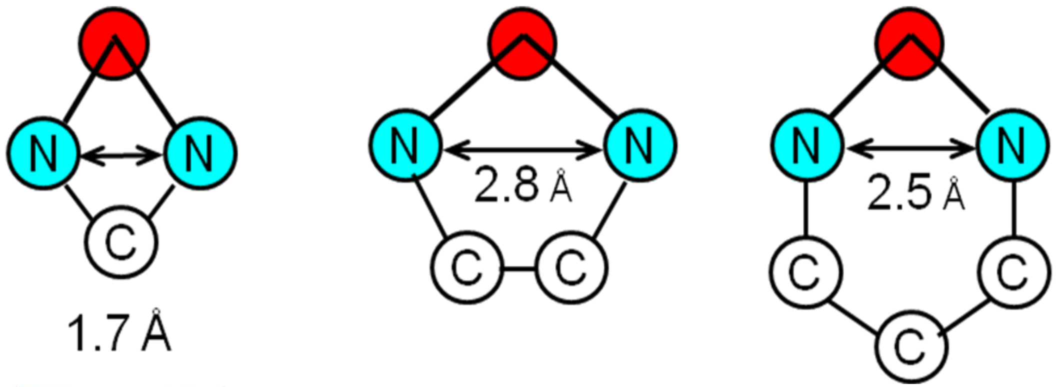
Exercise: Based on what we just learned, which ligand do you think will form the strongest complex with Co^{3+}? Rank them.

Answer: C > B > A > D > E

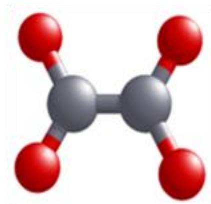
Exercise: Can anyone guess why this is the trend for the acidity with regard to the ammonia and the primary, secondary, and tertiary amines?

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.

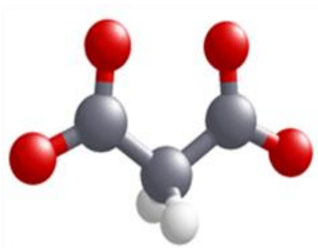
Improved stability in 5-membered rings: The chelate effect



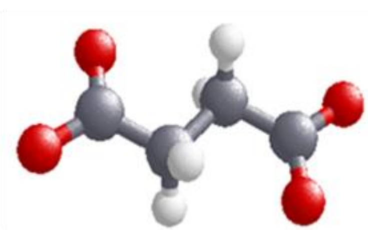
5-membered
oxalato

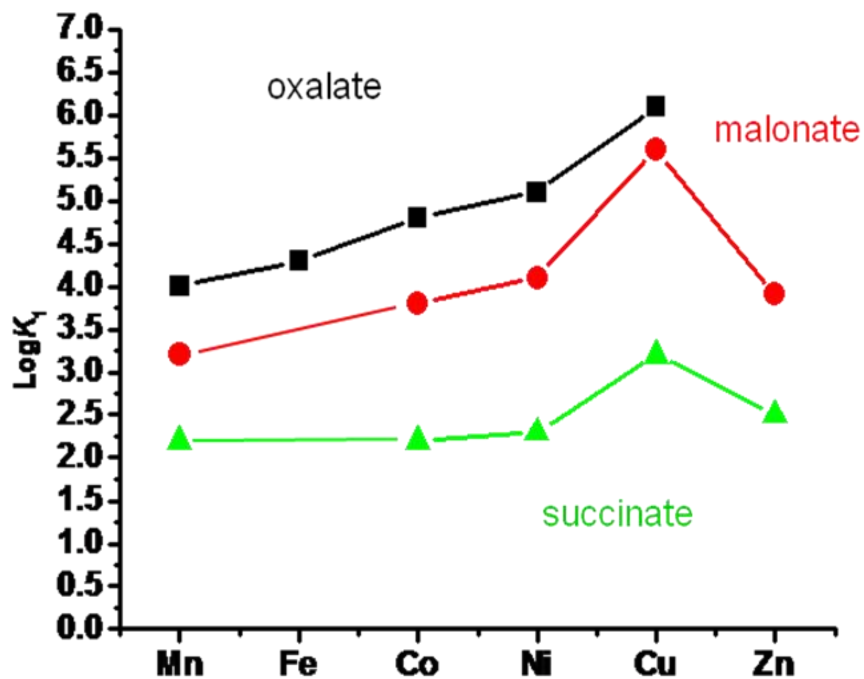


6-membered
malonato

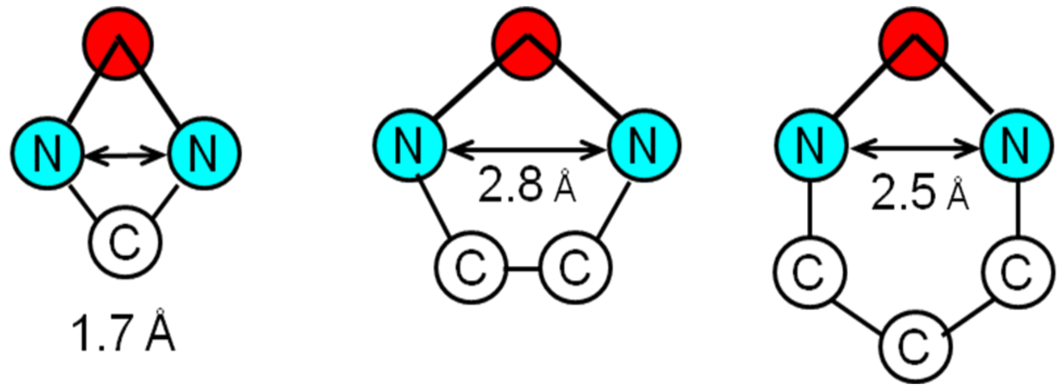


7-membered
succinato

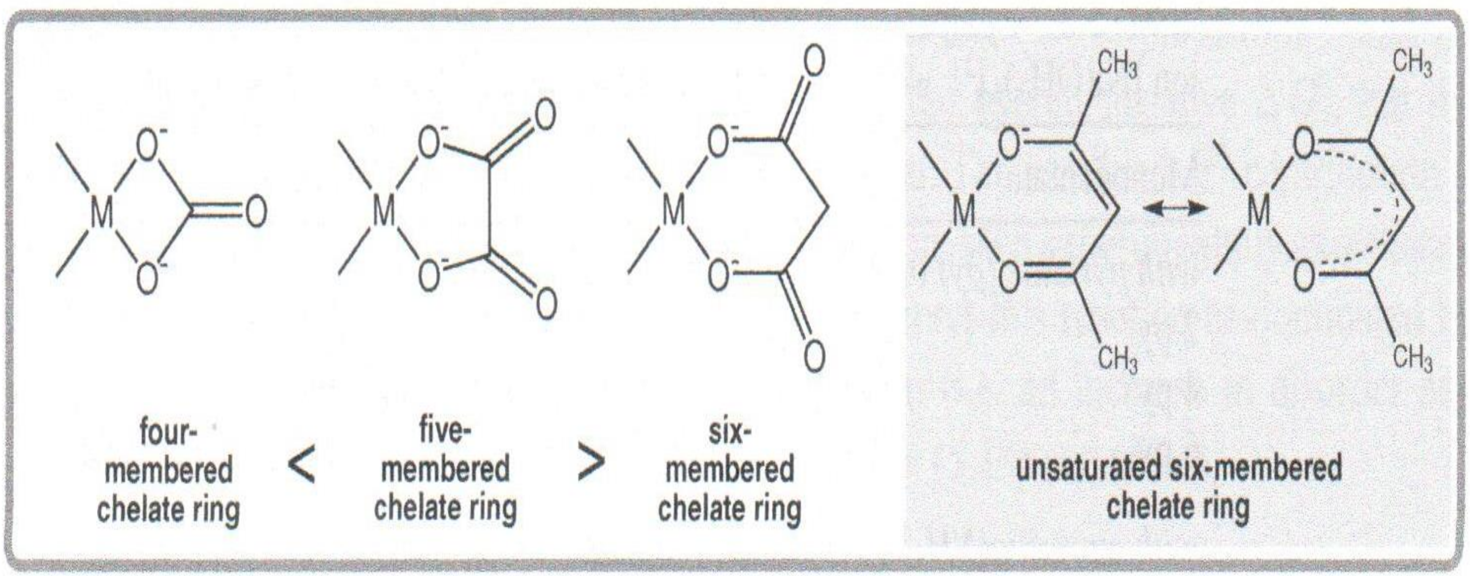




Improved stability in 5-membered rings: The chelate effect

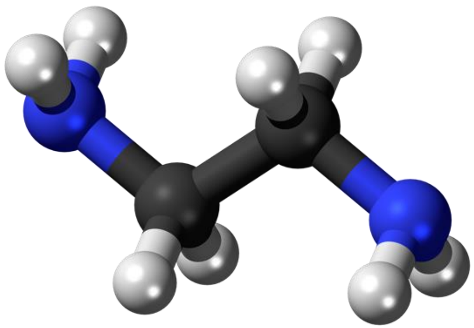


The exception – rings that contain unsaturated carbon atoms

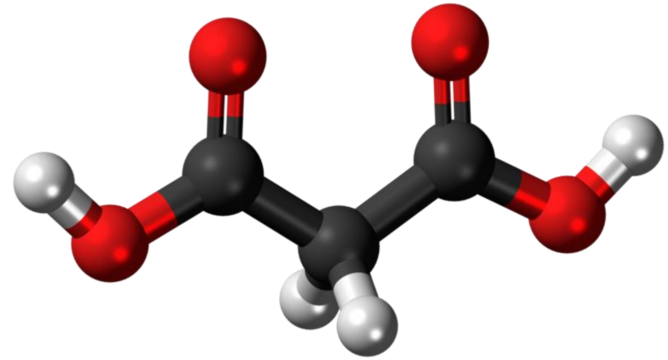


carbonato oxalato malanato acetylacetonato (acac)

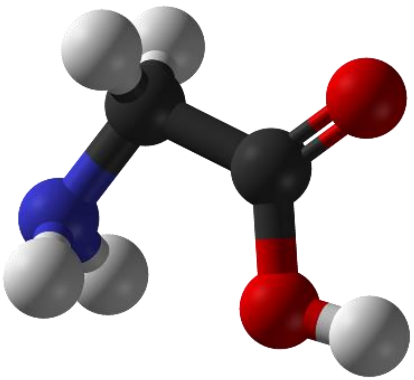
Exercise: Predict the order of stabilities for the following with Ni^{2+}



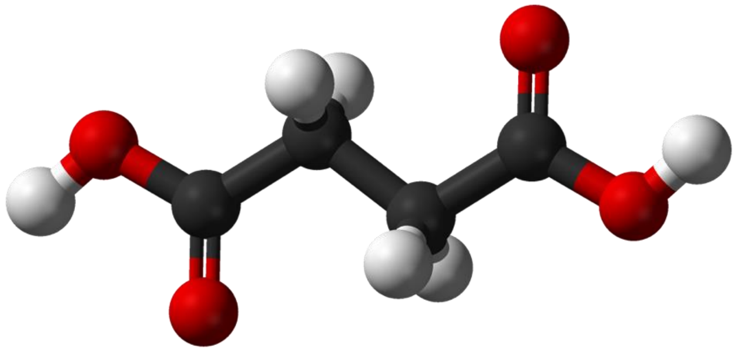
1). Ethylenediamine
NH_2-CH_2-CH_2-NH_2



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

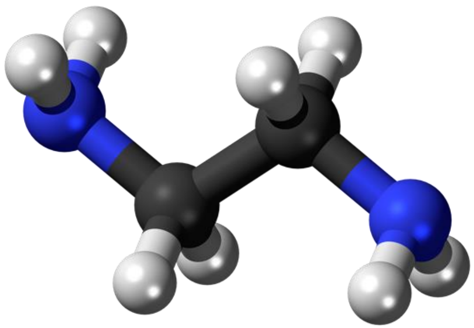


3). Glycine
NH_2-CH_2-CO_2^{-}

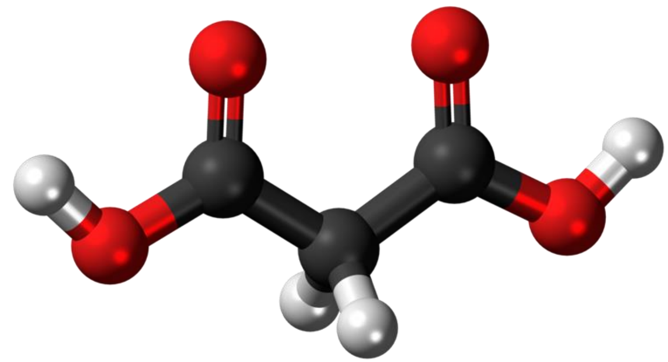


4). Succinic acid
$^{-}O_2C$-CH_2-CH_2-CO_2^{-}

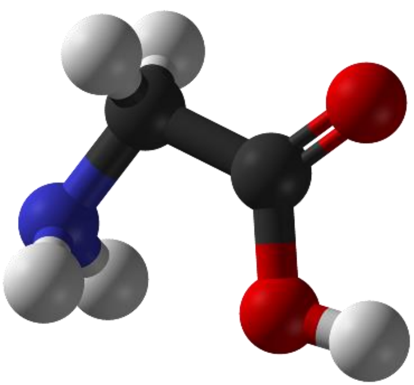
Exercise: Predict the order of stabilities for the following with Ni^{2+}



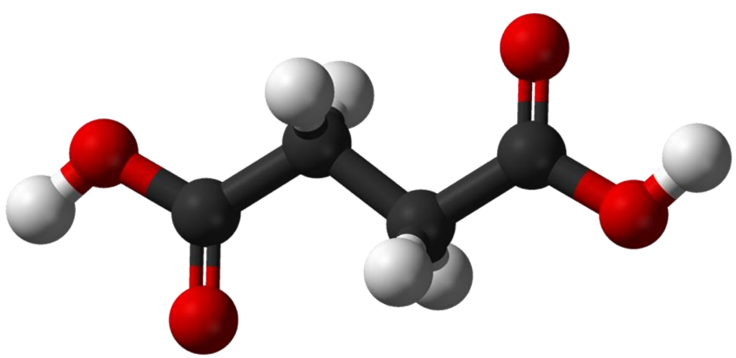
1). Ethylenediamine
NH_2-CH_2-CH_2-NH_2



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



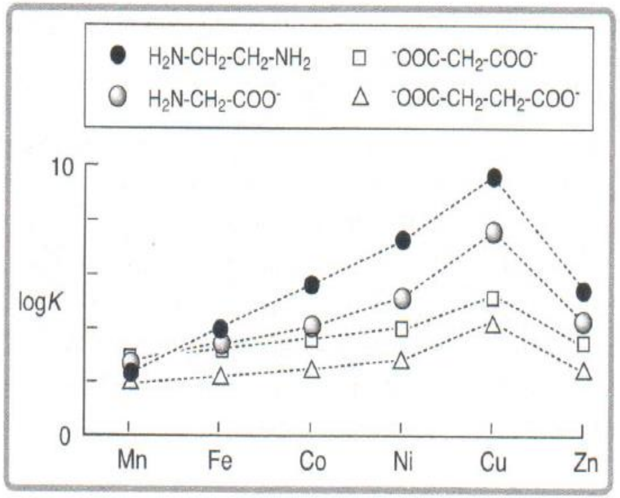
3). Glycine
NH_2-CH_2-CO_2^{-}

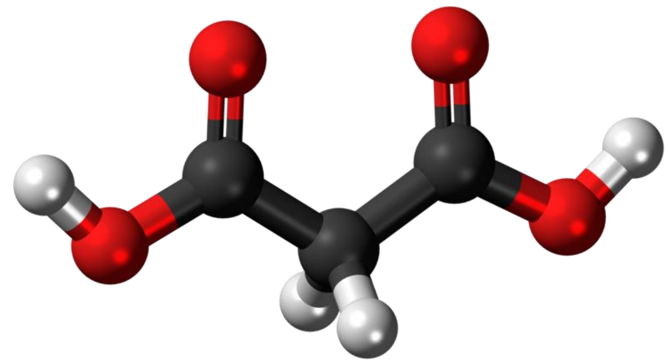


4). Succinic acid
$^{-}O_2C$-CH_2-CH_2-CO_2^{-}

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

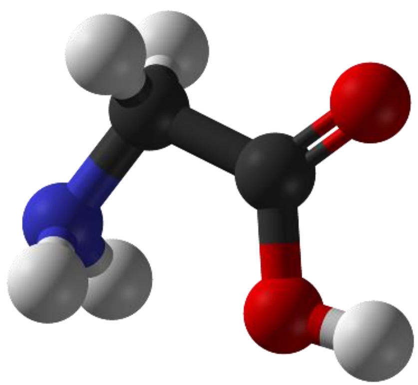
Exercise: Predict the order of stabilities for the following with Ni^{2+}





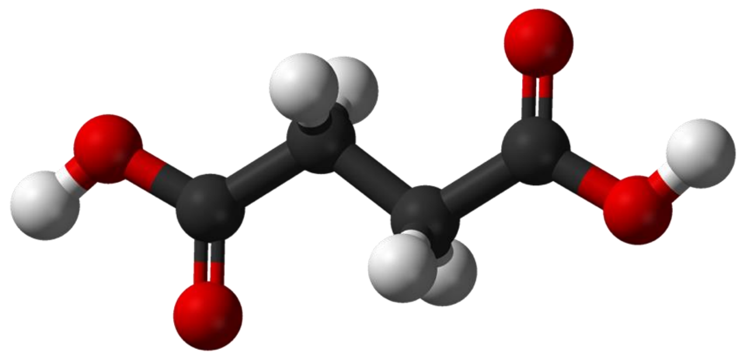
2). Malonic acid

$^{-}O_2C\text{-}CH_2\text{-}CO_2^{-}$



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

Answer: Yes according to the Irving Williams Series