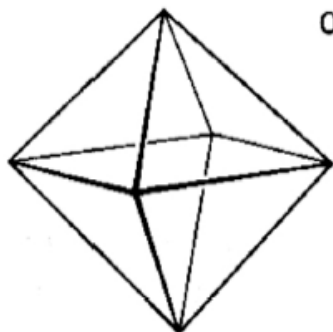
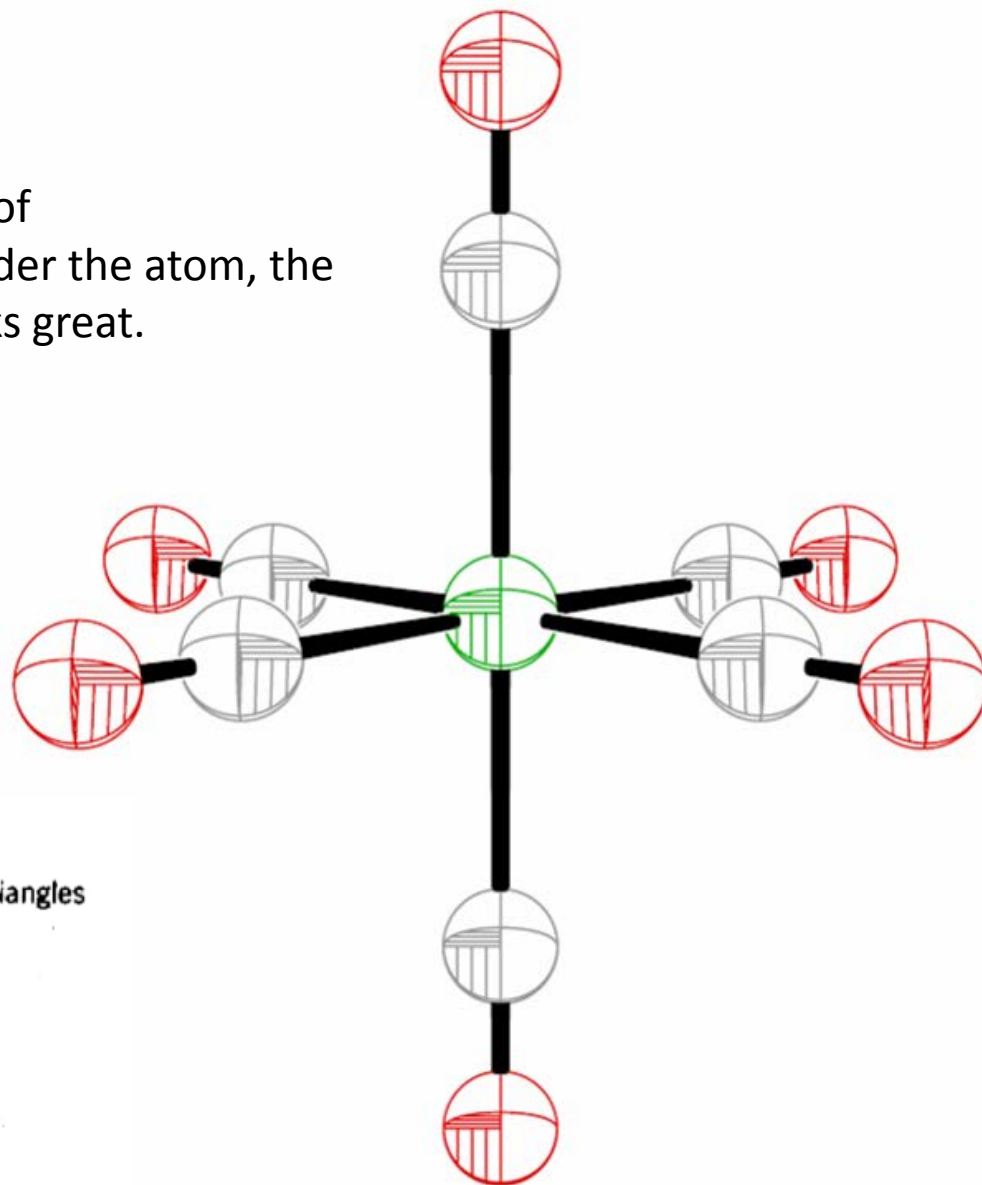


# ***Coordination Chemistry*** ***Transition Metal Complexes***

**Direct Application of Lewis AB and  
Hard/Soft AB “Theories”**

A TEP (Thermal Ellipsoid Plot) of  
a single molecule of  
tungsten hexacarbonyl,  $W(CO)_6$

Thermal ellipsoids indicate extent of  
thermal motion. The tighter, rounder the atom,  
the better the structure. This one looks great.



Octahedron  
Faces: 8 equilateral triangles  
Vertices: 6  
Edges: 12

## Overview of Transition Metal Complexes

1. The coordinate covalent or dative bond applies
2. Lewis bases are called LIGANDS—all serve as  $\sigma$ -donors  
some are  $\pi$ -donors as well, and some are  $\pi$ -acceptors
3. Specific coordination number and geometries  
depend on metal and number of d-electrons
4. HSAB theory useful
  - a) Hard bases stabilize high oxidation states
  - b) Soft bases stabilize low oxidation states

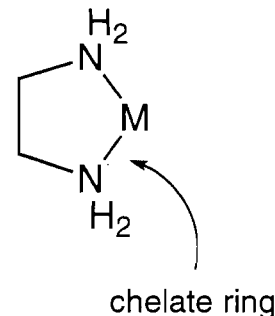
# Properties of Transition Metal Complexes

1. Highly colored (absorb light in visible, transmit light which eye detects)
2. Metals may exhibit multiple oxidation states
3. Metals may exhibit paramagnetism dependent on metal oxidation state and on ligand field.
4. Reactivity includes:
  - A) Ligand exchange processes:**
    - i) Associative ( $S_N2$ ; expanded coordination no.)
    - ii) Dissociative ( $S_N1$ ; slow step is ligand loss)
  - B) Redox Processes**
    - i) inner sphere atom transfer;
    - ii) outer sphere electron processes)
    - iii) Oxidative Addition and Reductive Elimination

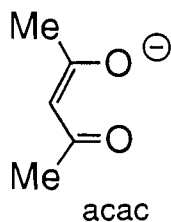
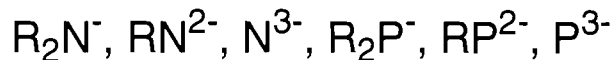
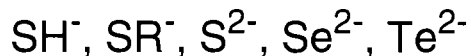
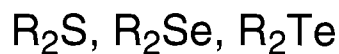
# Classification of Ligands (ALL are Lewis Bases)

## 3. Ligands

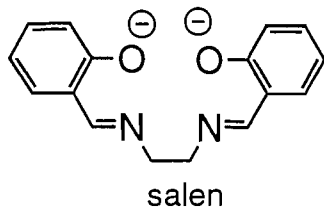
- $\sigma$ :  $\text{NH}_3$ ,  $\text{NR}_3$ ,  $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  (en),  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ , ...  
 $\sigma$ -bonding only



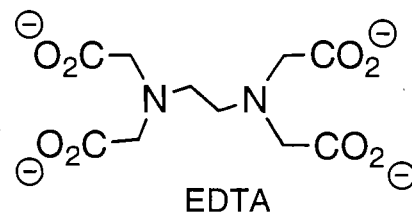
- $\sigma + \pi$  (lp):  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCO}^-$ ,  $\text{NCS}^-$ ,  $\text{N}_3^-$ , ...  
 $\pi$ -donors



bidentate chelate

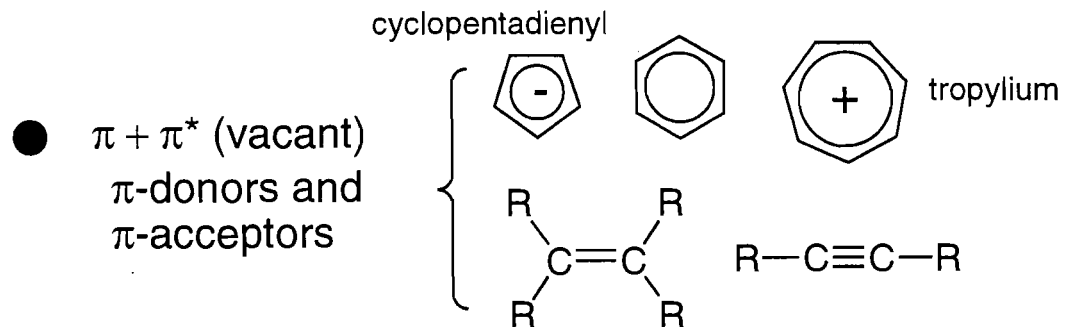
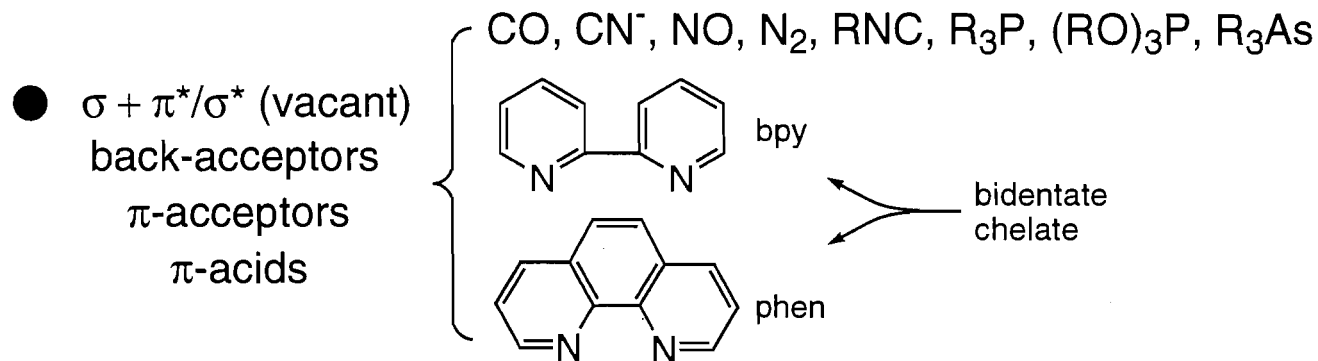


tetradentate chelate



hexadentate chelate

## Ligands, continued



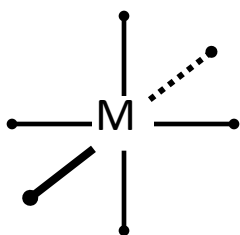
These ligands form *organometallic* molecules.

# Oxidation States Available to Essential Bulk and Trace Metals

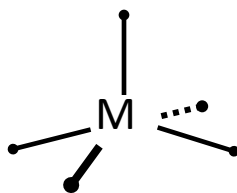
<i>Metal</i>	<i>Available Oxidation States</i>						
Na	1						
K	1						
Mg		2					
Ca		2					
V		2	(3)	(4)	(5)		
Cr		2	(3)	(4)	(5)	(6)	
Mn		2	3	4	(5)	(6)	(7)
Fe	<b>1</b>	2	3	4	(5)		
Co	1	2	3				
Ni	1	2	3				
Cu	1	2					
Zn		2					
Mo		2					

The parentheses indicate oxidation levels not normally found in biological molecules.

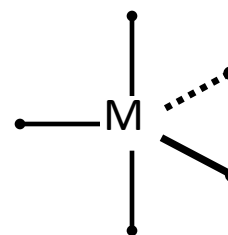
# Common Coordination Geometries



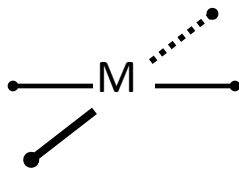
octahedral (Oh)



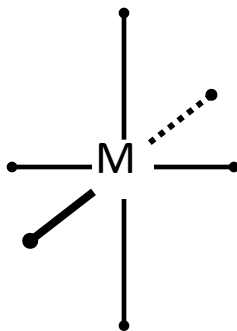
square pyramid (sp)



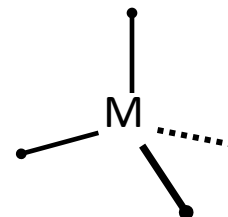
trigonal bipyramidal (tbp)



square planar (sp)



tetragonal (tet)



tetrahedral (Td)



## Preferred Coordination Numbers and Geometries for Selected Metal Ions

<i>Cation</i>	<i>C.N.</i>	<i>Geometry</i>	<i>Biological Ligands</i>
Na <sup>+</sup>	6	Octahedral	O, ether, hydroxyl, carboxylate
K <sup>+</sup>	6-8	Flexible	O, ether, hydroxyl, carboxylate
Mg <sup>2+</sup>	6	Octahedral	O, hydroxyl, phosphate
Ca <sup>2+</sup>	6-8	Flexible	O, carboxylate, carbonyl, (phosphate)
Mn <sup>2+</sup> (d <sup>5</sup> )	6	Octahedral	O, carboxylate, phosphate N, imidazole
Mn <sup>3+</sup> (d <sup>4</sup> )	6	Tetragonal	O, carboxylate, phosphate, hydroxide
Fe <sup>2+</sup> (d <sup>6</sup> )	4	Tetrahedral	S, thiolate
	6	Octahedral	O, carboxylate, alkoxide, oxide, phenolate N, imidazole, porphyrin
Fe <sup>3+</sup> (d <sup>5</sup> )	4	Tetrahedral	S, thiolate
	6	Octahedral	O, carboxylate, alkoxide, oxide, phenolate N, imidazole, porphyrin
Co <sup>2+</sup> (d <sup>7</sup> )	4	Tetrahedral	S, thiolate N, imidazole
	6	Octahedral	O, carboxylate N, imidazole
Ni <sup>2+</sup> (d <sup>8</sup> )	4	Square planar	S, thiolate N, imidazole, polypyrrole (F-430)
	6	Octahedral	uncommon
Cu <sup>1+</sup> (d <sup>10</sup> )	4	Tetrahedral	S, thiolate, thioether N, imidazole
Cu <sup>2+</sup> (d <sup>9</sup> )	4	Tetrahedral	S, thiolate, thioether N, imidazole
Cu <sup>2+</sup> (d <sup>9</sup> )	4	Square planar	O, carboxylate N, imidazole
	6	Tetragonal	O, carboxylate N, imidazole
Zn <sup>2+</sup> (d <sup>10</sup> )	4	Tetrahedral	O, carboxylate, carbonyl S, thiolate N, imidazole
	5	Square pyramidal	O, carboxylate, carbonyl N, imidazole

## 4. Electron Configurations of Atoms and Common Oxidation States of the First Transition Series

Free Atom	Oxidation States			Atom in Molecule	
Sc(4s <sup>2</sup> 3d <sup>1</sup> )	--	Sc <sup>3+</sup> (d <sup>0</sup> )	--	--	--
Ti(4s <sup>2</sup> 3d <sup>2</sup> )	--	Ti <sup>4+</sup> (d <sup>0</sup> )	Ti <sup>3+</sup> (d <sup>1</sup> )	Ti <sup>2+</sup> (d <sup>2</sup> )	Ti <sup>0</sup> (d <sup>4</sup> )
V(4s <sup>2</sup> 3d <sup>3</sup> )	V <sup>5+</sup> (d <sup>0</sup> )	V <sup>4+</sup> (d <sup>1</sup> )	V <sup>3+</sup> (d <sup>2</sup> )	V <sup>2+</sup> (d <sup>3</sup> )	V <sup>0</sup> (d <sup>5</sup> )
Cr(4s <sup>1</sup> 3d <sup>5</sup> )	Cr <sup>6+</sup> (d <sup>0</sup> )	Cr <sup>3+</sup> (d <sup>3</sup> )	Cr <sup>2+</sup> (d <sup>4</sup> )	--	Cr <sup>0</sup> (d <sup>6</sup> )
Mn(4s <sup>2</sup> 3d <sup>5</sup> )	Mn <sup>7+</sup> (d <sup>0</sup> )	Mn <sup>3+</sup> (d <sup>4</sup> )	Mn <sup>2+</sup> (d <sup>5</sup> )	--	Mn <sup>0</sup> (d <sup>7</sup> )
Fe(4s <sup>2</sup> 3d <sup>6</sup> )	Fe <sup>4+</sup> (d <sup>4</sup> )	Fe <sup>3+</sup> (d <sup>5</sup> )	Fe <sup>2+</sup> (d <sup>6</sup> )	--	Fe <sup>0</sup> (d <sup>8</sup> )
Co(4s <sup>2</sup> 3d <sup>7</sup> )	--	Co <sup>3+</sup> (d <sup>6</sup> )	Co <sup>2+</sup> (d <sup>7</sup> )	Co <sup>1+</sup> (d <sup>8</sup> )	Co <sup>0</sup> (d <sup>9</sup> )
Ni(4s <sup>2</sup> 3d <sup>8</sup> )	--	Ni <sup>3+</sup> (d <sup>7</sup> )	Ni <sup>2+</sup> (d <sup>8</sup> )	Ni <sup>1+</sup> (d <sup>9</sup> )	Ni <sup>0</sup> (d <sup>10</sup> )
Cu(4s <sup>1</sup> 3d <sup>10</sup> )	--	Cu <sup>3+</sup> (d <sup>8</sup> )	Cu <sup>2+</sup> (d <sup>9</sup> )	Cu <sup>1+</sup> (d <sup>10</sup> )	--
Zn(4s <sup>2</sup> 3d <sup>10</sup> )	--	Zn <sup>2+</sup> (d <sup>10</sup> )	--	--	--

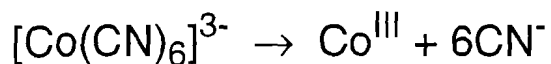
# Oxidation State Assignment of Metal

## 5. Oxidation State

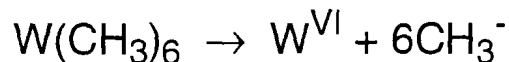
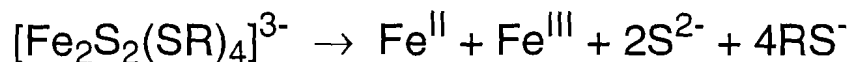
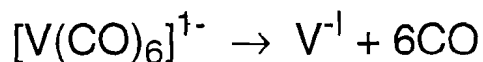
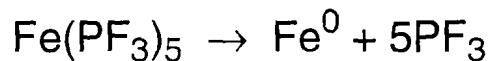
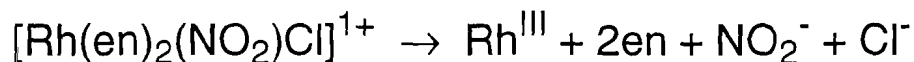
$$\text{ox. state} = z - \sum_N \text{L charge}$$

ligand removed from complex with closed shell configuration

examples:



positive oxidation states usually written as Roman numerals



An oxidation state is a formalism which affords that  $d^n$  configuration consistent with molecular properties.

So, how do we mix these ligands and metals with their various oxidation states to get stable molecules?

1. Hard/Soft Acid Base Approach to stability
2. Knowledge of preferred coordination numbers and geometries

# Hard/Soft Classification of Lewis Acids and Bases

	Acids	Bases
Hard	$H^+$ , $Li^+$ , $Na^+$ , $K^+$ , $Mg^{2+}$ , $Ca^{2+}$ , $Mn^{2+}$ $Al^{3+}$ , $Ln^{3+}$ , $Cr^{3+}$ , $Co^{3+}$ , $Fe^{3+}$ , $VO^{2+}$ , $MoO^{3+}$ , $SO_3$ , $CO_2$	$H_2O$ , $ROH$ , $NH_3$ , $RNH_2$ $RCO_2^-$ , $Cl^-$ , $F^-$ $PO_4^{3-}$ , $HPO_4^{2-}$ , $H_2PO_4^-$ , $SO_4^{2-}$
Intermediate	$Fe^{2+}$ , $Co^{2+}$ , $Ni^{2+}$ , $Cu^{2+}$ , $Zn^{2+}$ $Pb^{2+}$ , $Sn^{2+}$ , $SO_2$ , $NO^+$ , $Ru^{2+}$	Imidazole, pyridine
Soft	$Cu^+$ , $Ag^+$ , $Au^+$ , $Tl^+$ , $Hg^+$ $Cd^{2+}$ , $Pd^{2+}$ , $Pt^{2+}$ , $Hg^{2+}$	$RSH$ , $R_2S$ $CN^-$ , $I^-$ $S_2O_3^{2-}$

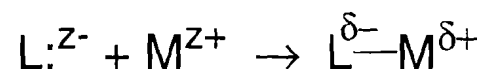
Higher charge/smaller ionic radii: **harder**

Lower charge/larger ionic radii: **softer**

# Linus Pauling's Electroneutrality Principle

## 6. Electroneutrality Principle:

In any molecule, bonding electrons are distributed in such a way that individual atoms are as close to electroneutrality as possible.



Metal-ligand bond formation tends to reduce +ve charge on M (and -ve charge on  $L^{Z-}$ ), with the result that the *actual* charge on M is much below that corresponding to its oxidation state. The oxidation state conveys the  $d^n$  configuration of the coordinated metal.

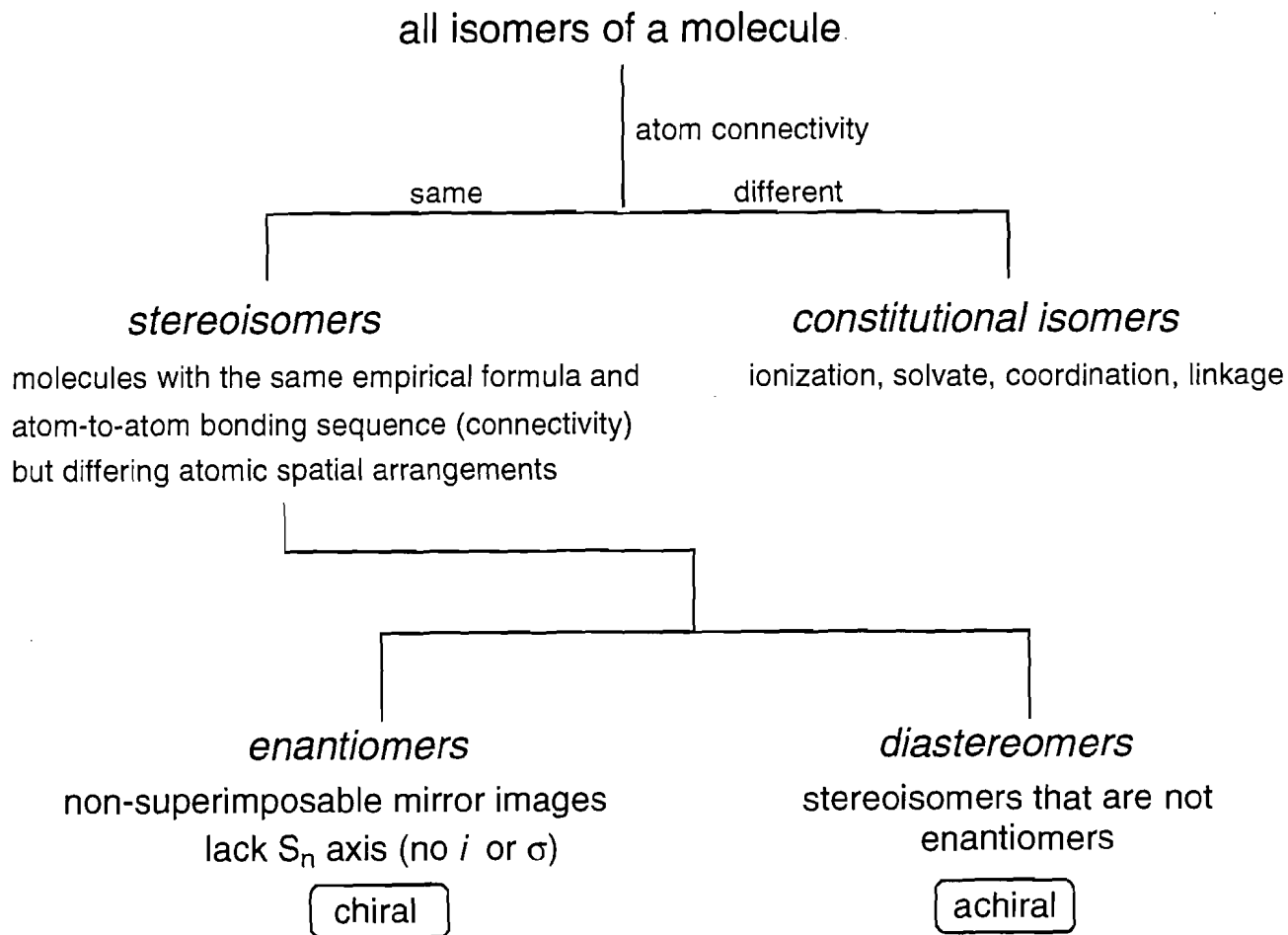
- high oxidation states stabilized by anionic  $\pi$ -donor ligands of electronegative atoms
- low oxidation states stabilized by neutral  $\pi$ -acceptor ligands

examples:

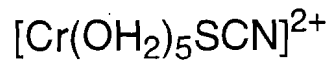
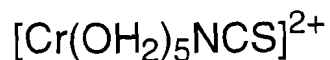
	"high"	"low"
Ti	$[\text{TiF}_6]^{2-}$ , $\text{TiO}_2$	$\text{Ti}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2$
V	$[\text{VF}_6]^{2-}$ , $[\text{VOCl}_4]^{1-}$ , $[\text{VO}_2\text{Cl}_2]^{1-}$	$[\text{V}(\text{CO})_6]^{0,1-}$
Cr	$[\text{CrO}_4]^{2-}$ , $[\text{CrOCl}_4]^{1-}$ , $[\text{CrF}_6]^{2-}$	$[\text{Cr}(\text{CNR})_6]^{1+}$ , $\text{Cr}(\text{CO})_6$ , $[\text{Cr}(\text{CO})_5]^{2-}$
Mn	$[\text{MnO}_4]^{1-,2-}$ , $[\text{MnCl}_6]^{2-}$	$\text{Mn}(\text{CO})_5\text{Cl}$ , $\text{Mn}_2(\text{CO})_{10}$ , $[\text{Mn}(\text{CO})_5]^{1-}$
Fe	$[\text{FeO}_4]^{2-}$ , $[\text{FeCl}_4]^{1-}$	$\text{Fe}(\text{CO})_5$ , $\text{Fe}(\text{PF}_3)_5$ , $[\text{Fe}(\text{CO})_4]^{2-}$
Co	$[\text{CoF}_6]^{3-}$ , $[\text{Cr}(\text{en})_3]^{3+}$	$[\text{Co}(\text{CO})_4]^{1-}$ , $\text{Co}(\text{CO})_3\text{NO}$ , $\text{Co}_2(\text{CO})_8$ , $\text{Co}(\text{PR}_3)_3\text{Br}$
Ni	$[\text{NiF}_6]^{2-}$ , $[\text{Ni}(\text{diars})_2\text{Cl}_2]^{1+}$	$\text{Ni}(\text{CO})_4$ , $\text{Ni}(\text{PF}_3)_4$ , $\text{Ni}(\text{PR}_3)_3\text{Br}$ , $[\text{Ni}_2(\text{CN})_6]^{4-}$
Cu	$[\text{CuF}_6]^{3-}$	$[\text{Cu}(\text{CN})_2]^{1-}$ , $[\text{CuCl}_2]^{1-}$

At parity of ligand and coordination number, higher oxidation states become increasingly stable down a vertical group.

## ● Isomerism



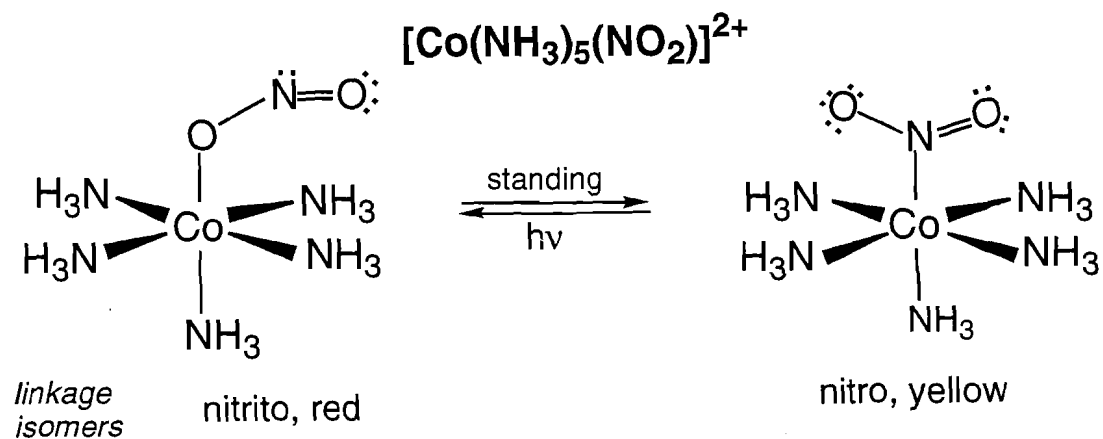
Examples:



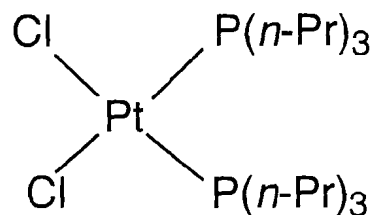
linkage isomers



## Linkage isomers or Ambi-dentate ligands



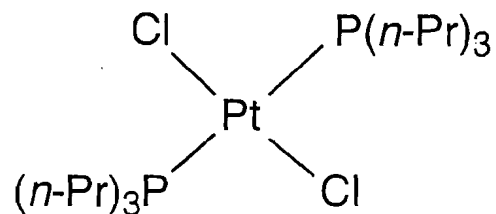
## Structural isomers: diastereomers



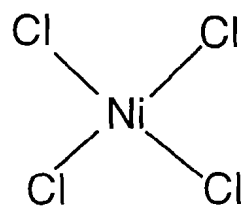
cis-planar  $C_{2v}$



*2 diastereomers*



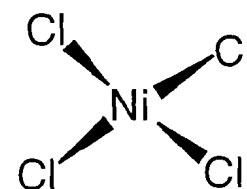
trans-planar  $D_{2h}$



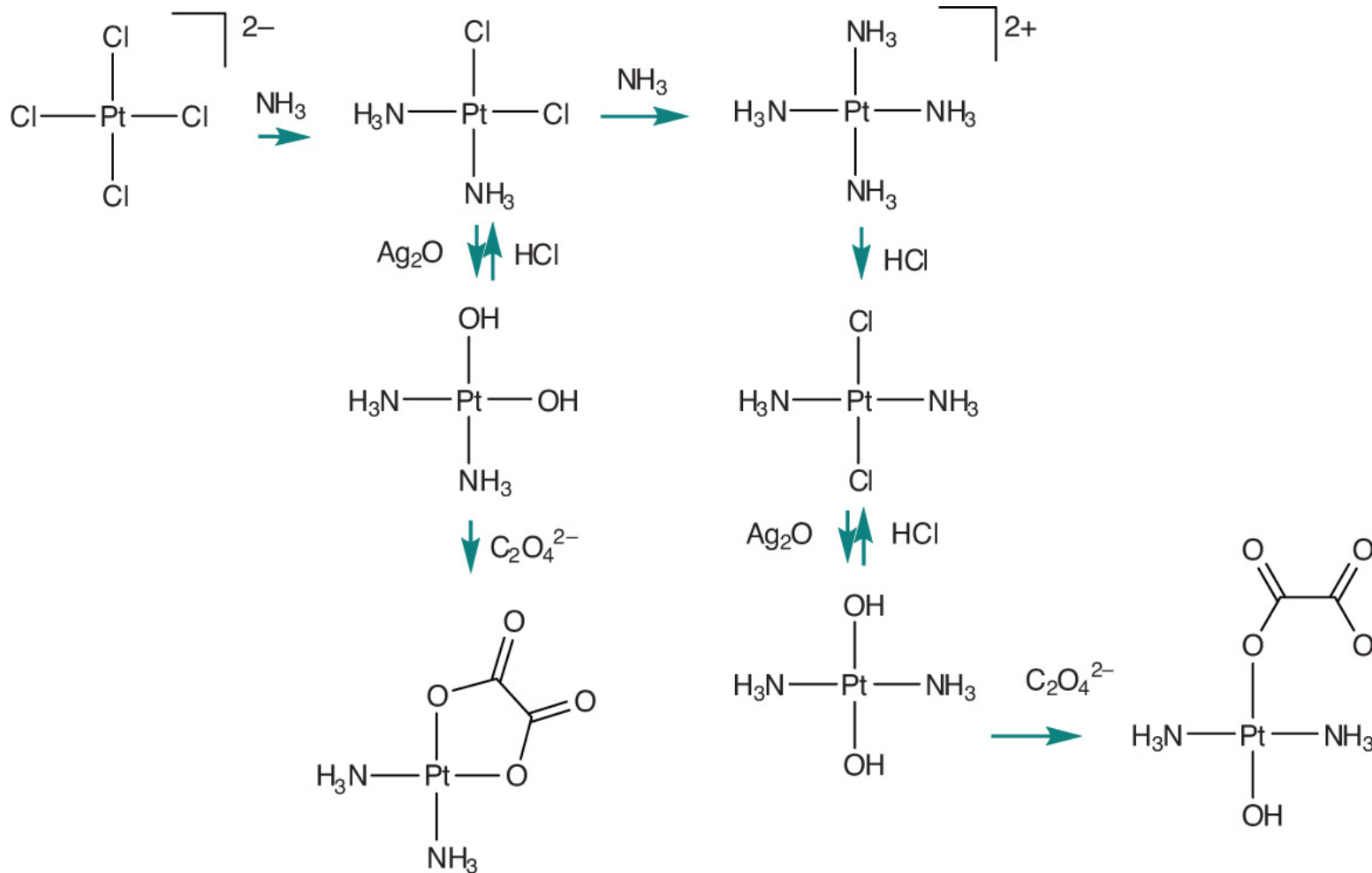
planar  $D_{4h}$   
 $K^+$  salt

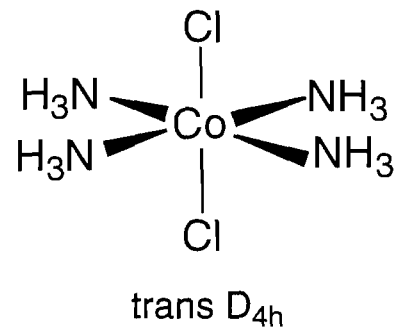
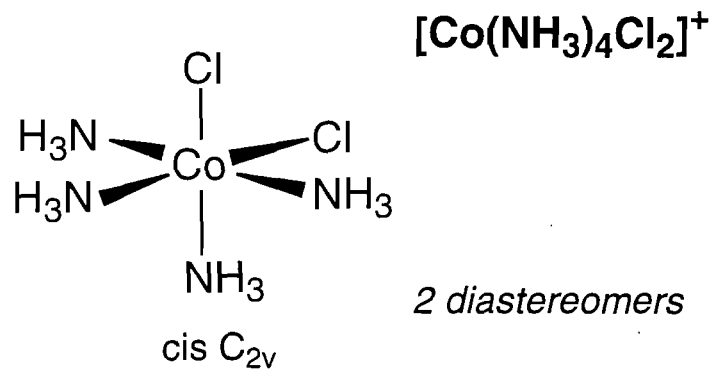


*2 diastereomers*

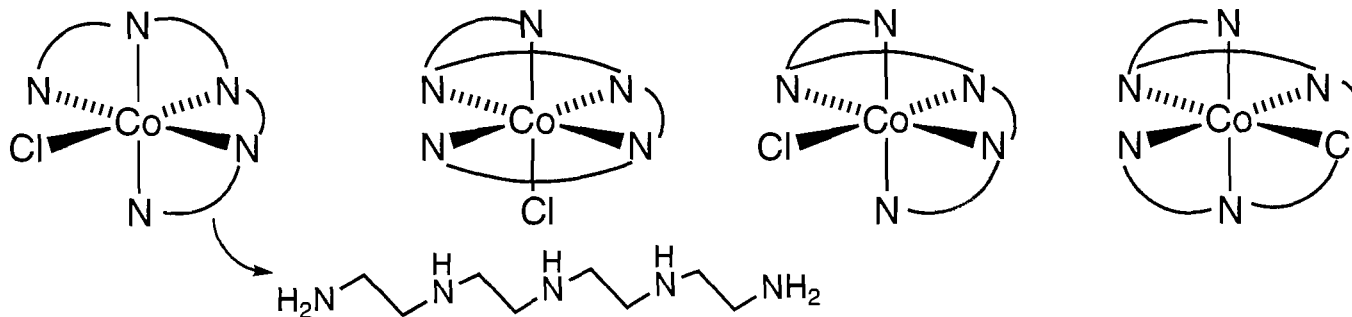


tetrahedral  $T_d$   
 $Ph_4As^+$  salt





*2 diastereomers*



each isomer is chiral

So, How do we measure stability?

Formation Constant:

$$\Delta G^{\circ} = -RT \ln K_{eq}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S$$

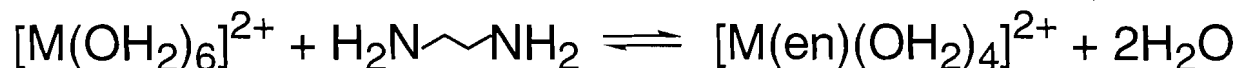
## ● Irving-Williams Stability Order

For the reactions  $M + nL \rightleftharpoons ML_n$ , the following order of stability constants holds under the indicated conditions (very few exceptions).



conditions: M has same charge and is high-spin

does not include Cu(II) binding of axial ligands

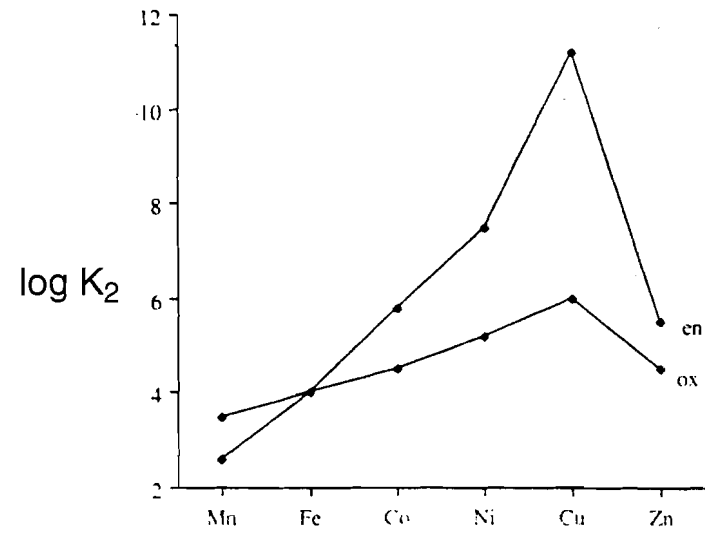


quantity	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
log K <sub>1</sub> (M <sup>-1</sup> )	2.79	4.33	5.94	7.70	10.7	5.78
-ΔG <sub>298</sub> (kcal/mol)	3.80	5.90	8.10	10.5	14.6	7.89
-ΔH (kcal/mol)*	2.80	5.09	6.88	8.89	13.0	6.69
TΔS <sub>298</sub> (kcal/mol)	1.0	0.81	1.2	1.6	1.6	1.2

\*determined calorimetrically

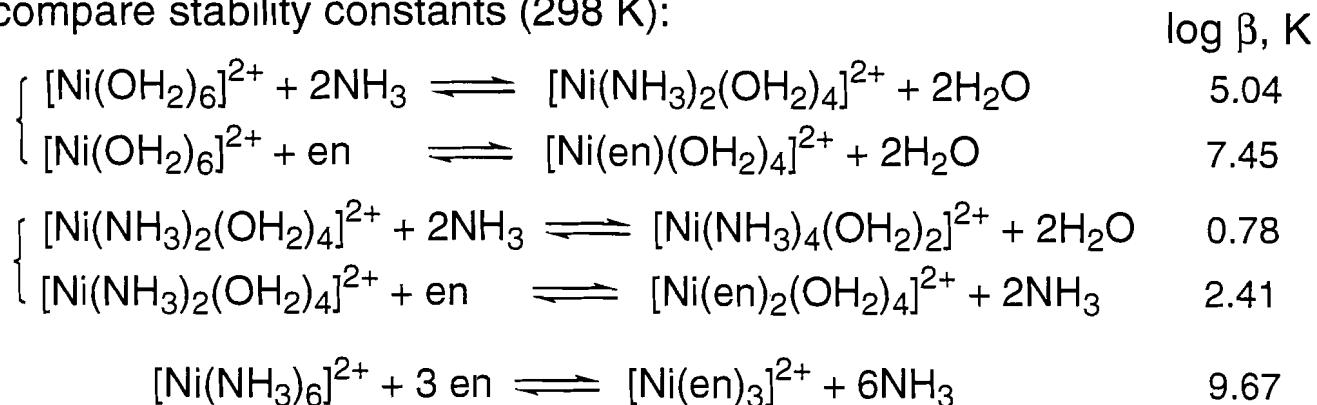
Reaction is favored  
enthalpically and  
entropically, but with  
 $|\Delta H| \gg T\Delta S$

Similar results for  
 $K_2$  reaction.



## ● Chelate effect

compare stability constants (298 K):



$$\Delta H = -2.89 \text{ kcal/mol} \quad \text{small favorable contribution}$$

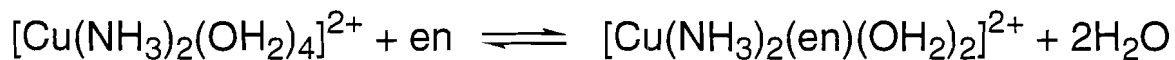
$$\Delta H_{SE} = -2.75 \text{ kcal/mol}$$

$$T\Delta S = 13.2 \text{ kcal/mol}$$

entropy increase (4→7 particles) dominates reaction

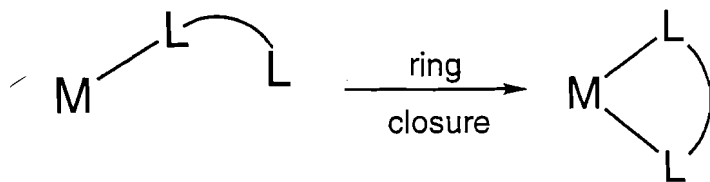
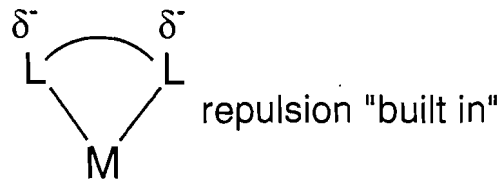
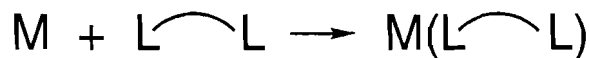
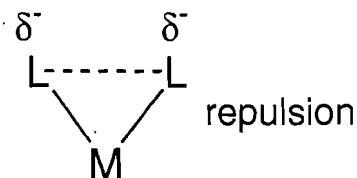
(even though  $\text{NH}_3$  more strongly solvated than en)





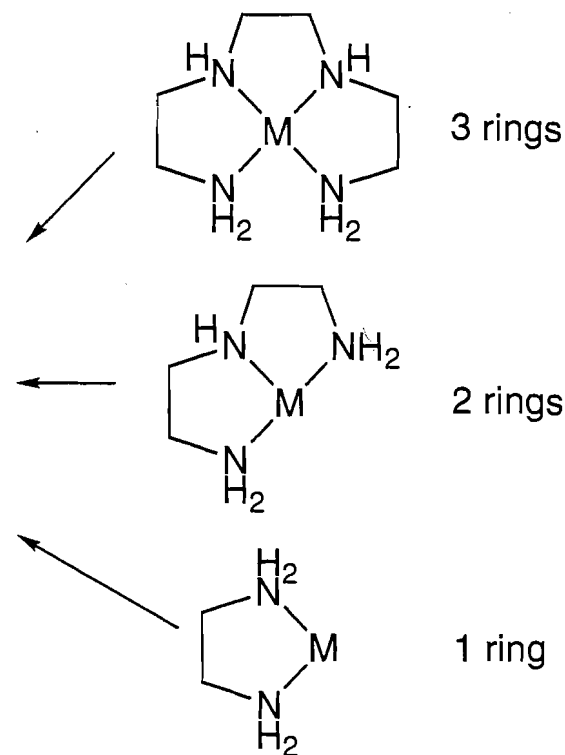
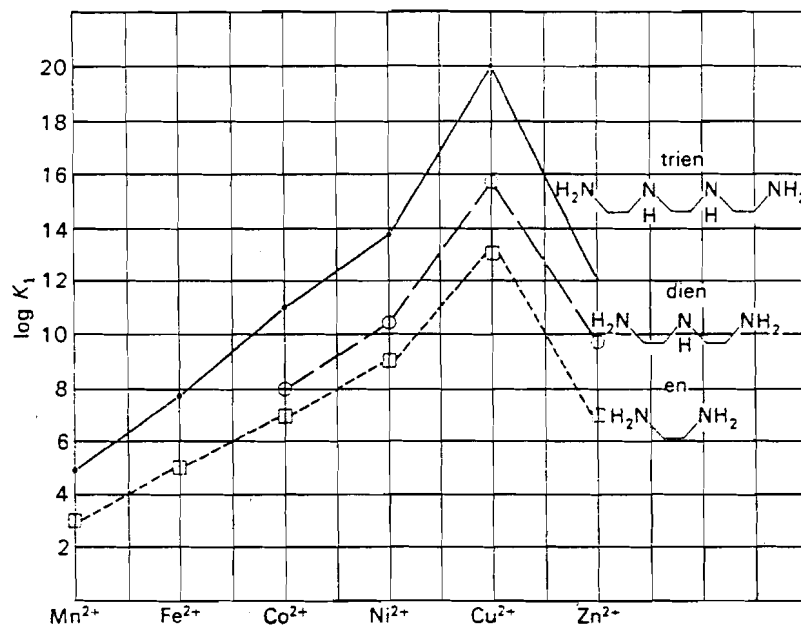
$$\Delta G = -3.70 \text{ kcal/mol} \quad \Delta H = -1.91 \text{ kcal/mol} \quad T\Delta S = 1.79 \text{ kcal/mol}$$

↑ favorable      ↑ (2 → 3 particles)

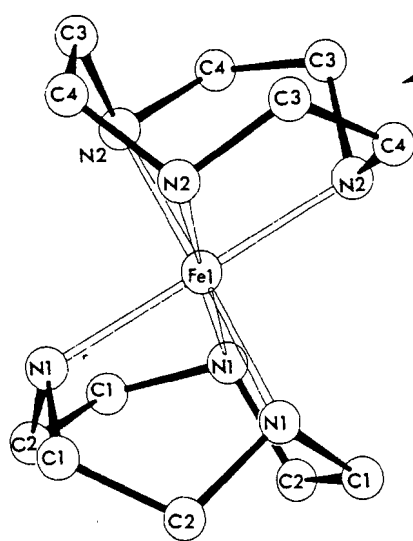


Once the first M-L bond is formed, there is a high probability the second bond will form because of the proximity of the other L atom. Corresponding probability is much lower with two unidentate ligands.

● number of chelate rings



Stability increases because enthalpy becomes increasingly negative (increased number of M–N bonds) and entropy increases (more water molecules released).



1,4,7-triazacyclononane (tacn)  
3 rings/ligand

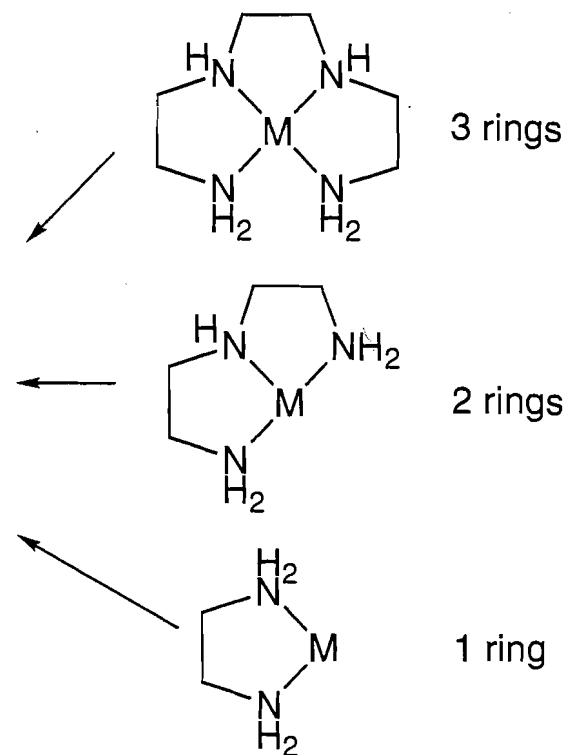
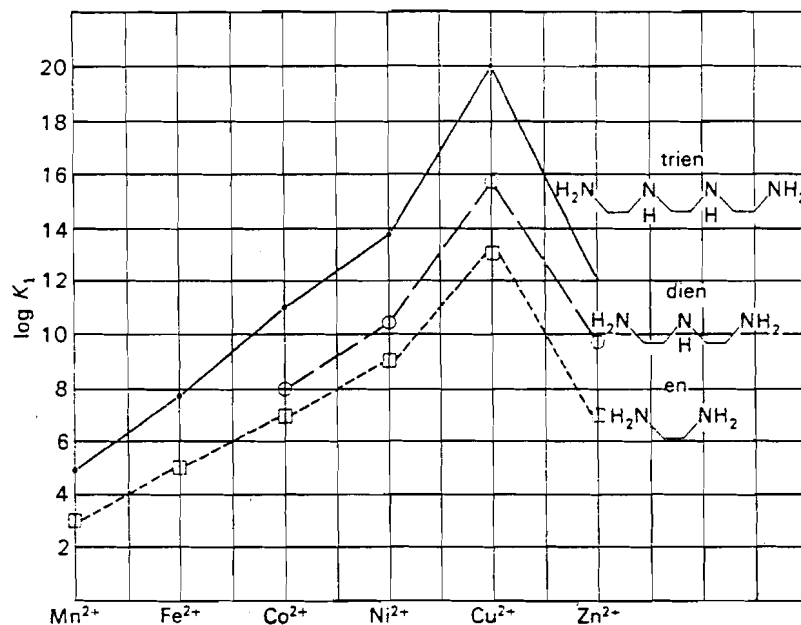
tacn forms relatively stable complexes  
with  $\text{M}^{2+,3+}$



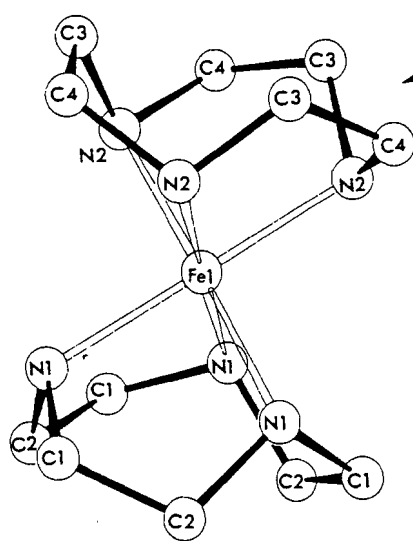
	log $K_1$
Ni(II)	16.24
Cu(II)	17.5
Zn(II)	11.6

favorable  $\Delta H$ ,  $\Delta S$ ;  
difficult to break M–N bonds because  
of semi-rigid ligand structure

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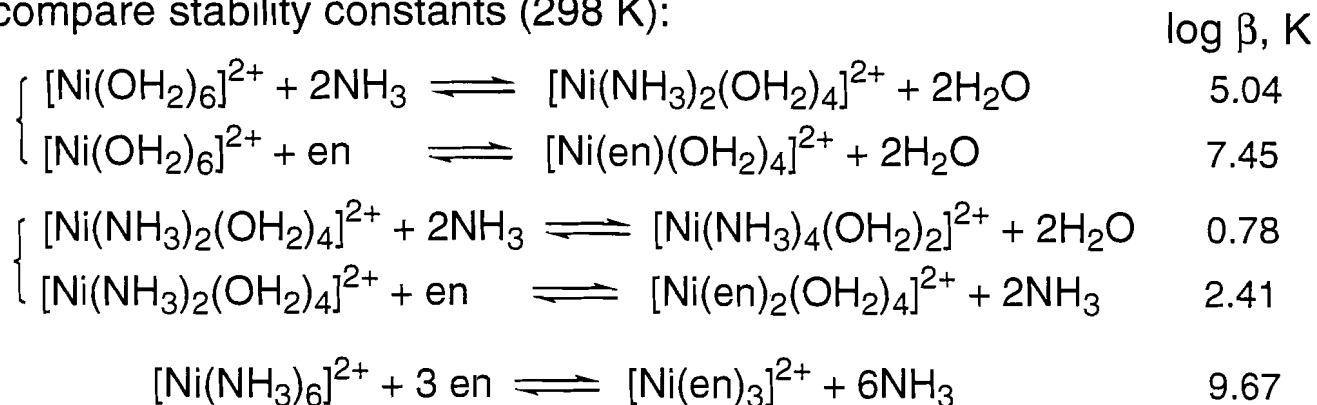


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## ● Chelate effect

compare stability constants (298 K):



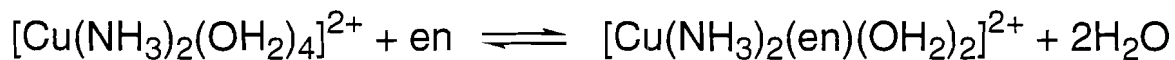
$$\Delta H = -2.89 \text{ kcal/mol} \quad \text{small favorable contribution}$$

$$\Delta H_{SE} = -2.75 \text{ kcal/mol}$$

$$T\Delta S = 13.2 \text{ kcal/mol}$$

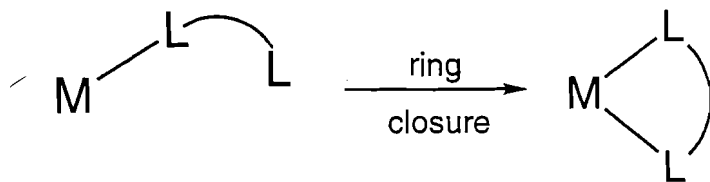
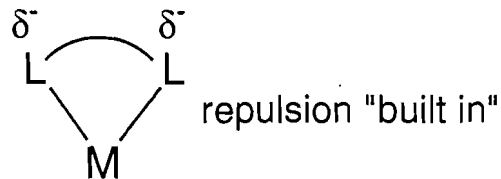
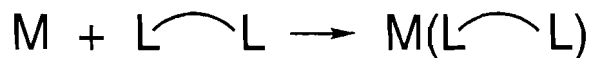
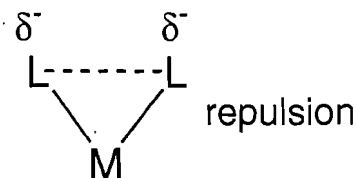
entropy increase (4→7 particles) dominates reaction

(even though  $\text{NH}_3$  more strongly solvated than en)



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