

# METALS

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General Chemistry I, Lecture Series 12

Pengxin Liu

Reading:

OGB8 §8, YY §18



# Outline

- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
  - Nature of coordination bonding: Lewis acid-base reaction
  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - Coordination Theory
    - Crystal-field theory
    - Hybridization Valence Bond theory
    - Ligand-field theory
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

# Scope

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
H																	He	
Li	Be						Transition metals											
Na	Mg																	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	C	N	O	F	Ne	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ga	Ge	As	Se	Br	Kr	
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	In	Sn	Sb	Te	I	Xe	
Fr	Ra	**	f-block metals										Tl	Pb	Bi	Po	At	Rn
*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

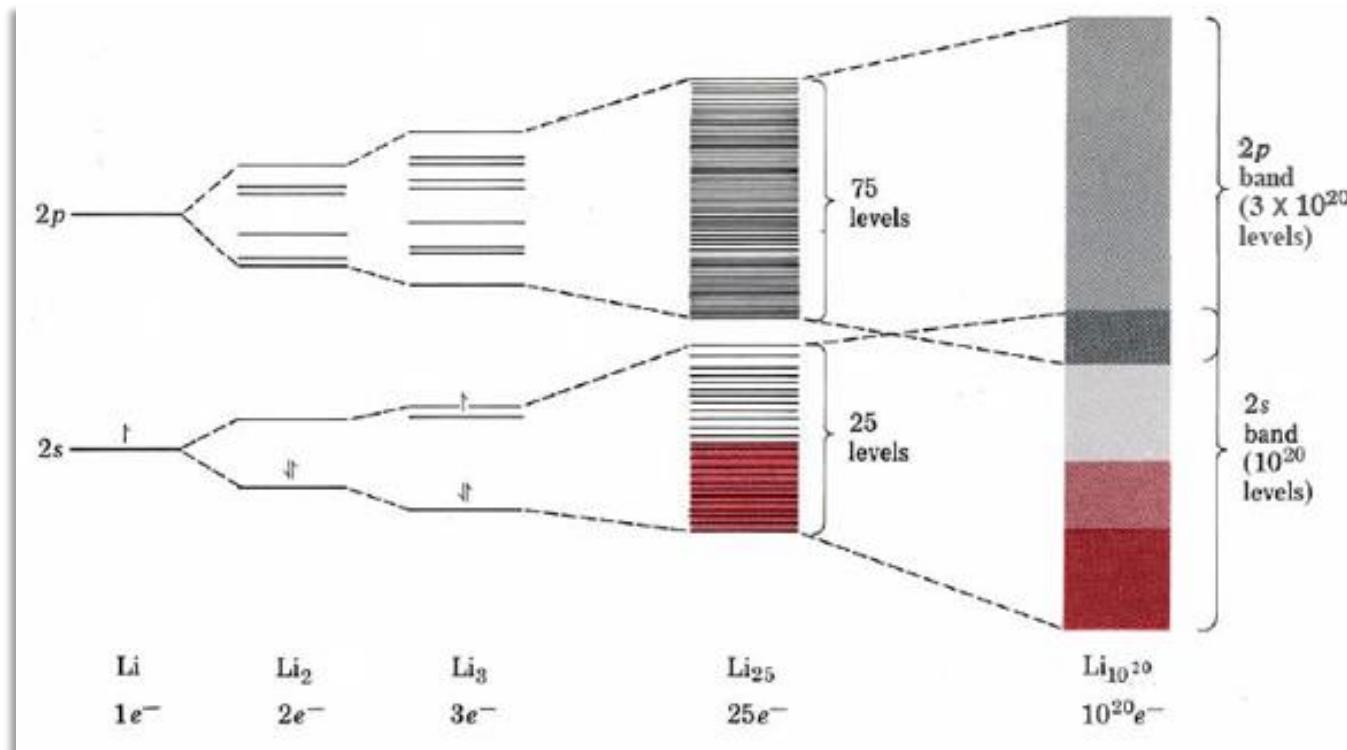
# Metallurgy



Type of Ore	Examples
Native Metals	Cu, Ag, Au, As, Sb, Bi, Pd, Pt
Oxides	$\text{Al}_2\text{O}_3$ , $\text{Fe}_2\text{O}_3$ , $\text{Fe}_3\text{O}_4$ , $\text{SnO}_2$ , $\text{MnO}_2$ , $\text{TiO}_2$ , $\text{FeO}\bullet\text{Cr}_2\text{O}_3$ , $\text{FeO}\bullet\text{WO}_3$ , $\text{Cu}_2\text{O}$ , $\text{ZnO}$
Carbonates	$\text{CaCO}_3$ , $\text{CaCO}_3\bullet\text{MgCO}_3$ , $\text{MgCO}_3$ , $\text{FeCO}_3$ , $\text{PbCO}_3$ , $\text{BaCO}_3$ , $\text{SrCO}_3$ , $\text{ZnCO}_3$ , $\text{MnCO}_3$ , $\text{CuCO}_3\bullet\text{Cu}(\text{OH})_2$
Sulfides	$\text{Ag}_2\text{S}$ , $\text{Cu}_2\text{S}$ , $\text{CuS}$ , $\text{PbS}$ , $\text{ZnS}$ , $\text{HgS}$ , $\text{FeS}\bullet\text{CuS}$ , $\text{FeS}_2$ , $\text{Sb}_2\text{S}_3$ , $\text{Bi}_2\text{S}$ , $\text{MoS}_2$ , $\text{NiS}$ , $\text{CdS}$
Halides	$\text{NaCl}$ , $\text{KCl}$ , $\text{AgCl}$ , $\text{KCl}\bullet\text{MgCl}_2\bullet 6\text{H}_2\text{O}$ , $\text{NaCl}$ and $\text{MgCl}_2$ in seawater
Sulfates	$\text{BaSO}_4$ , $\text{SrSO}_4$ , $\text{PbSO}_4$ , $\text{CaSO}_4\bullet 2\text{H}_2\text{O}$ , $\text{CuSO}_4\bullet 2\text{Cu}(\text{OH})_2$
Silicates	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , $\text{ZrSiO}_4$ , $\text{Sc}_2\text{Si}_2\text{O}_7$
Phosphates	$\text{LaPO}_4$ , $\text{LiF}\bullet\text{AlPO}_4$

# Metallic Bonding – Why Metal shine

Band theory of Solids: electrons jumping among these levels can have any energy within a broad band from the lowest to highest.

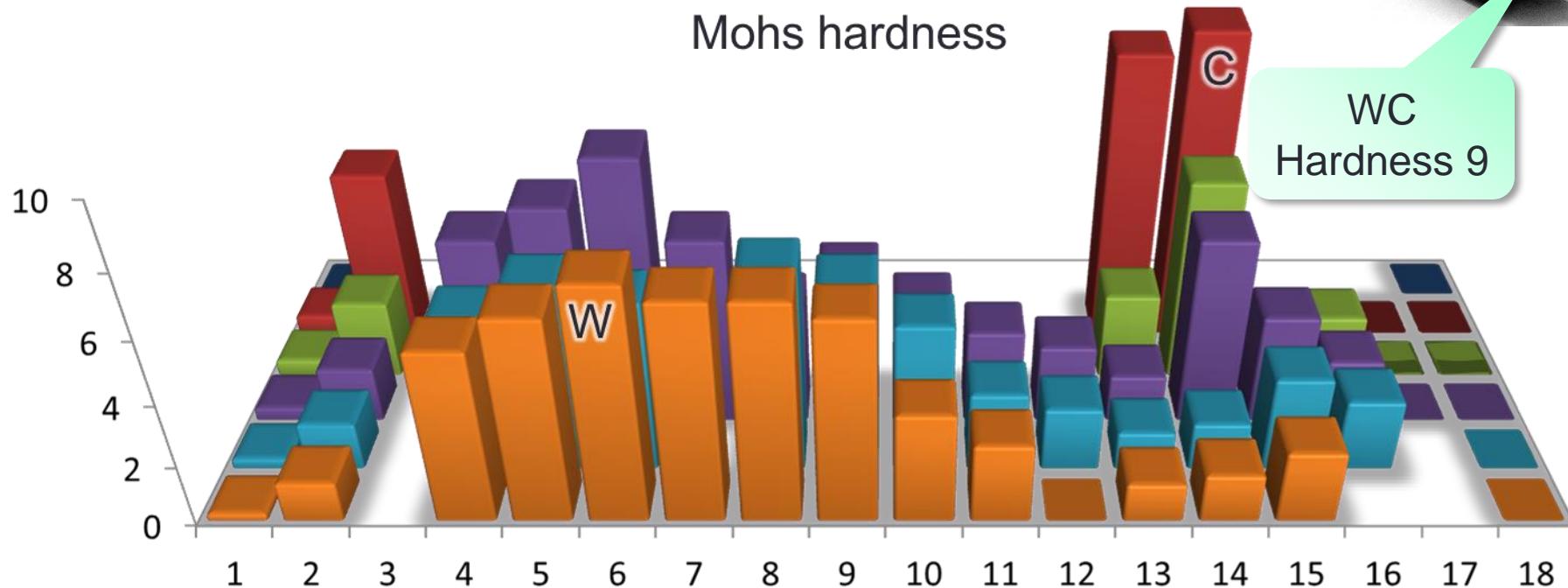


Explain: shining; high electrical conductance and temperature dependency; high thermal conductance; hardness; melting (boiling) point trends

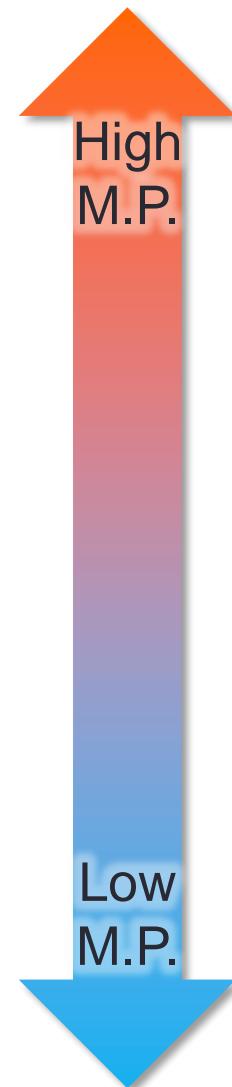
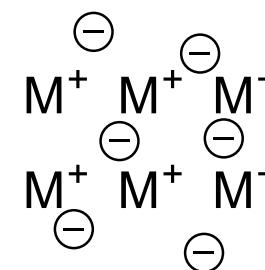
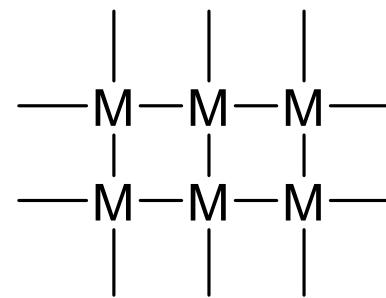
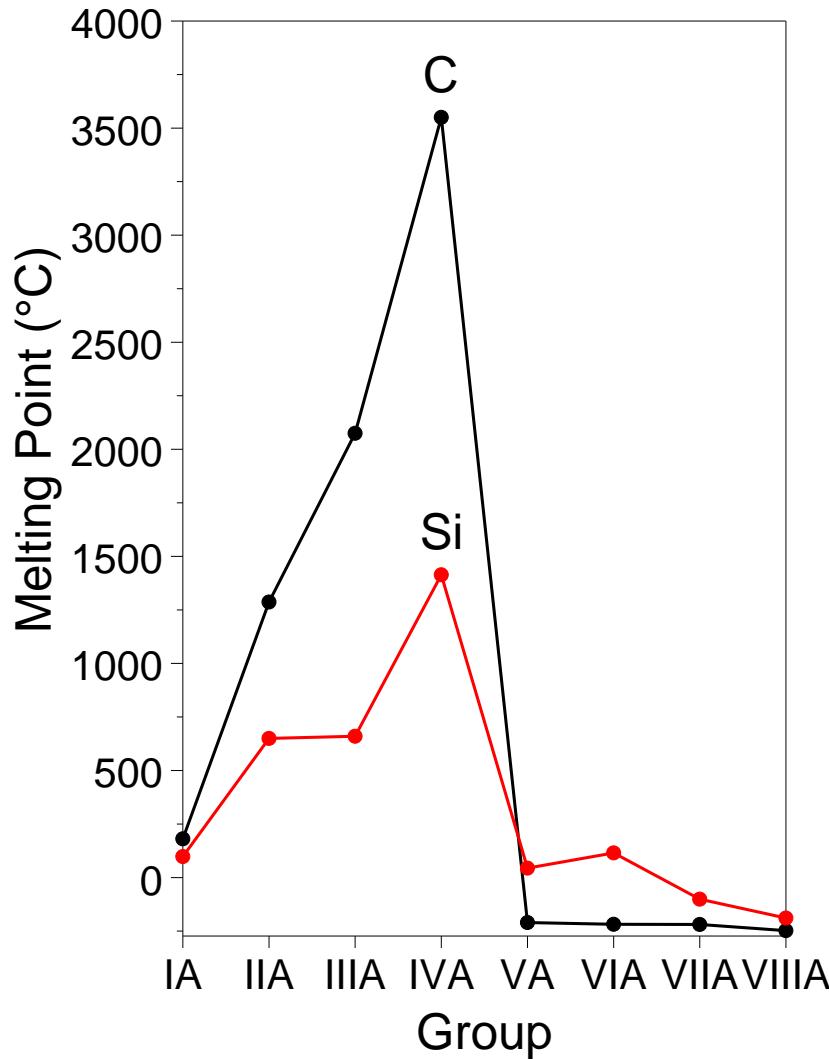
# Mechanical Properties

- Hardness
- Ductility & malleability 延展性
- Thermal expansion 热膨胀

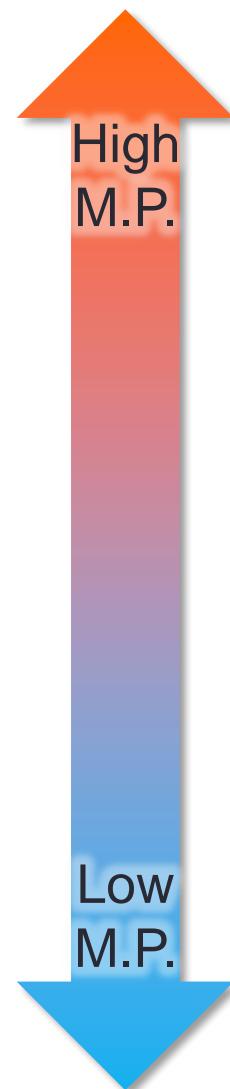
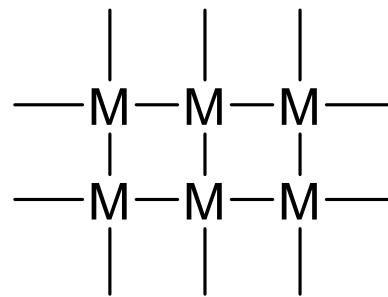
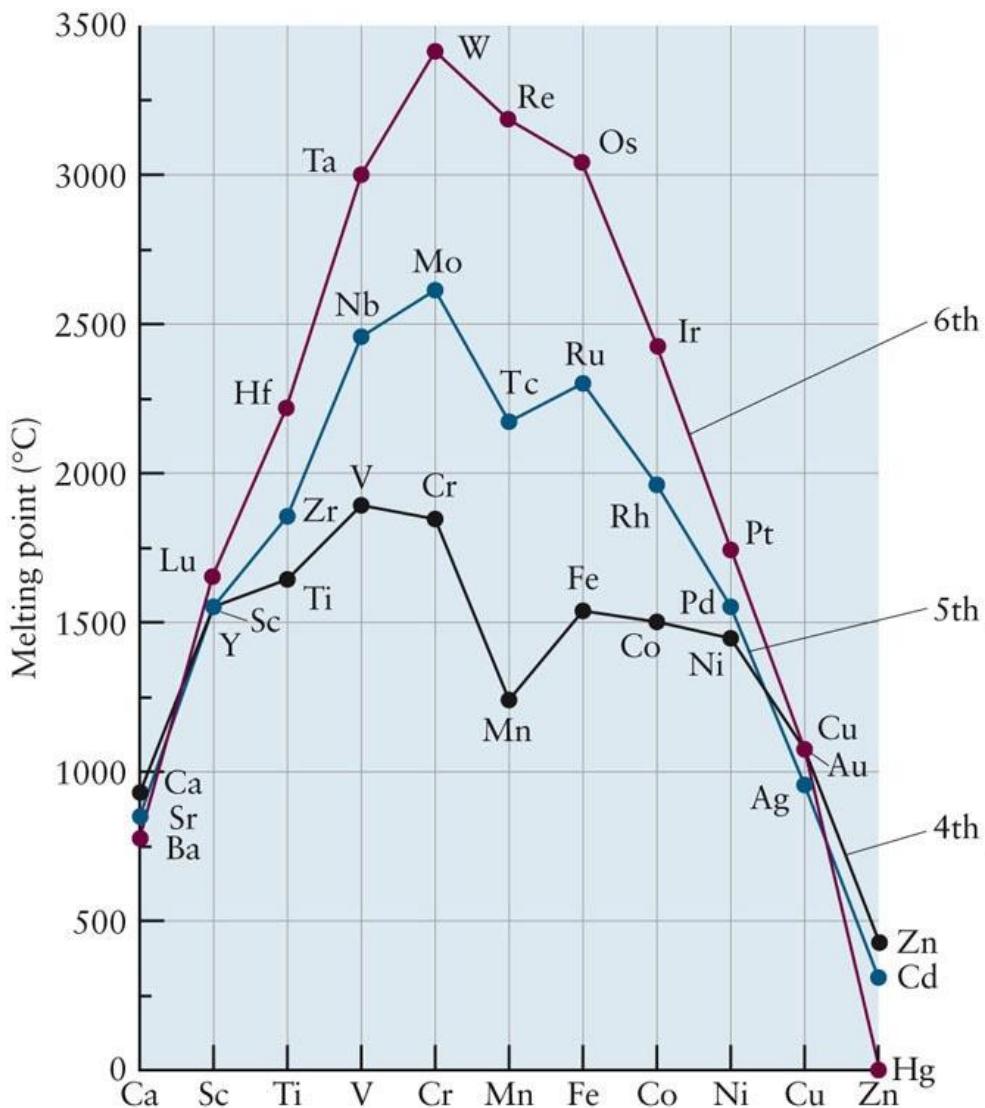
Hg: 60.4 ppm/K  
W: 4.5 ppm/K

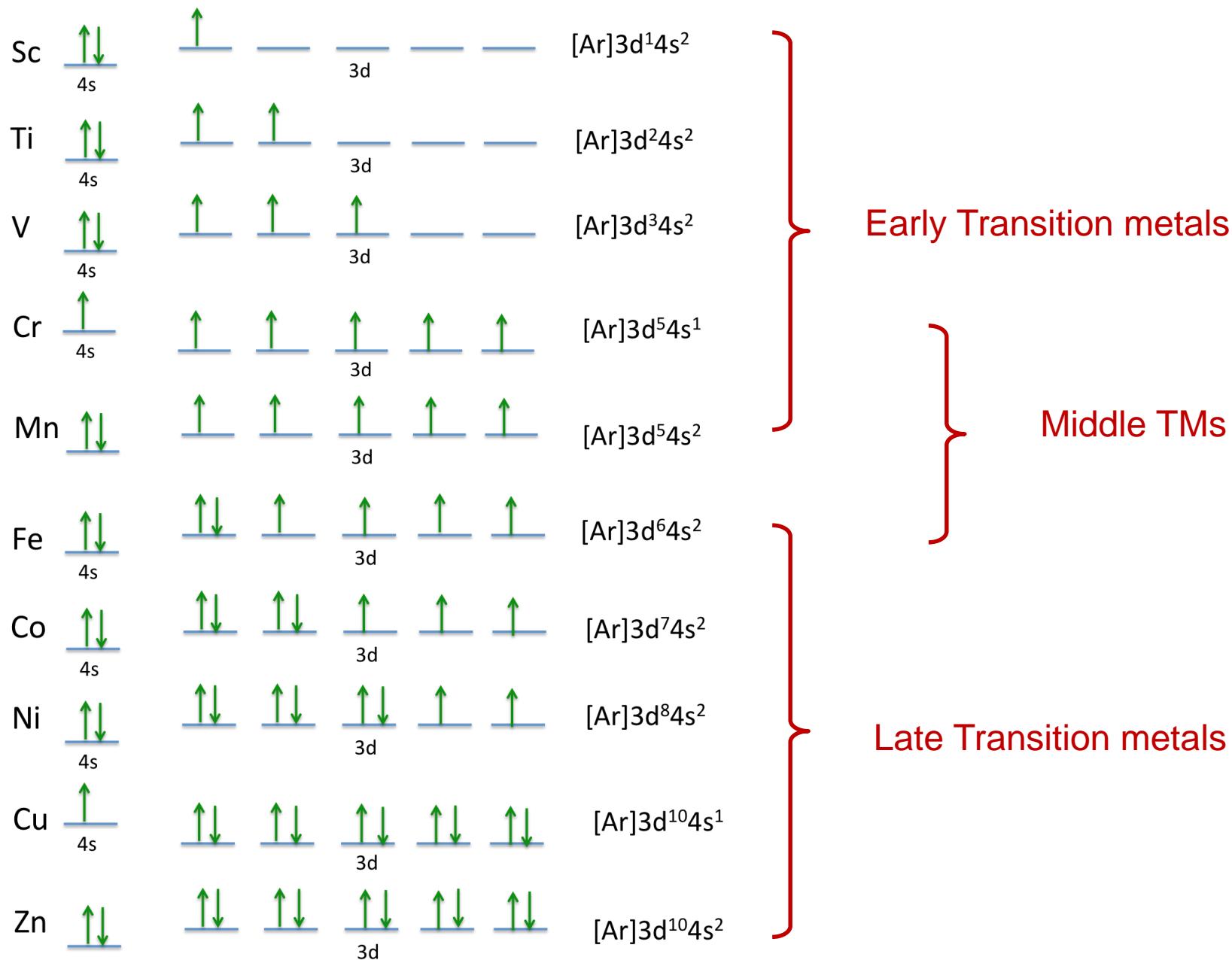


# Physical Properties: Melting Points (1)



# Physical Properties: Melting Points (2)





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    - Magnetism
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# Scope

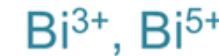
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
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K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	C	N	O	F	Ne	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ga	Ge	As	Se	Br	Kr	
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Fr	Ra	**	f-block metals										Tl	Pb	Bi	Po	At	Rn
*	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
**	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr			

# Inert pair effect

13

14

15



The most stable oxide and chloride of Al are  $\text{Al}_2\text{O}_3$  and  $\text{AlCl}_3$  while the most stable oxides and Cl of Tl are  $\text{Tl}_2\text{O}$  and  $\text{TlCl}$ .

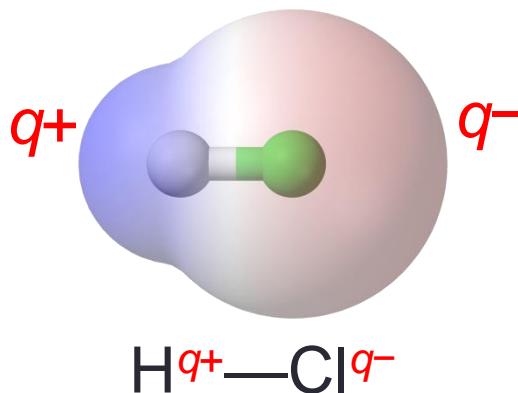
The higher ( $n^+$ ) oxidation state is favored for lighter elements so that the order of preference is



The lower ( $n - 2$ )<sup>+</sup> oxidation state is favored for heavier elements

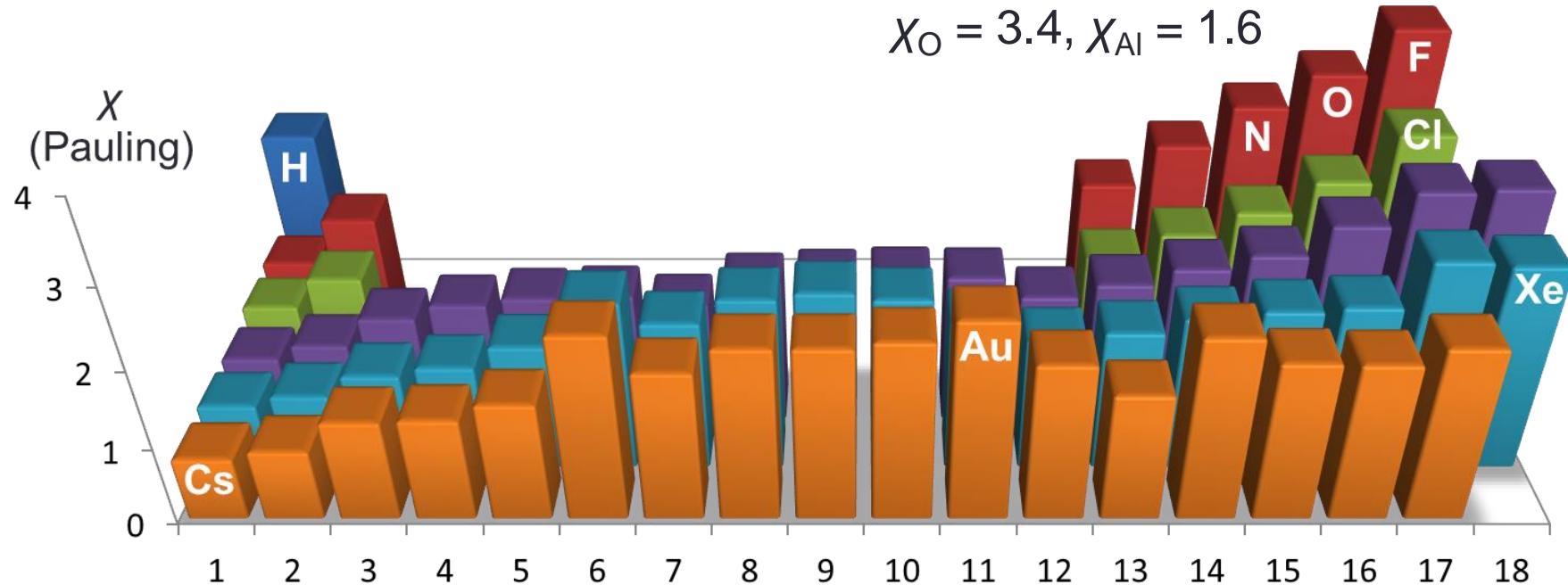


# Calculating Electronegativities

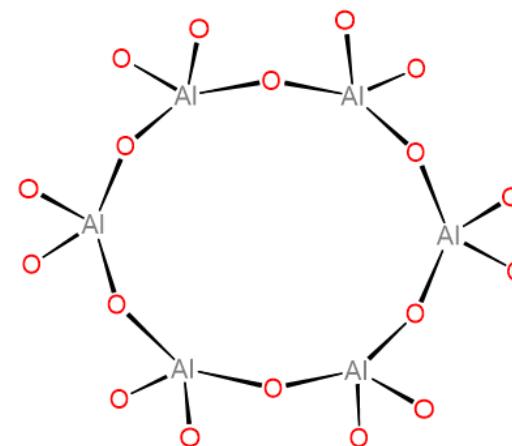
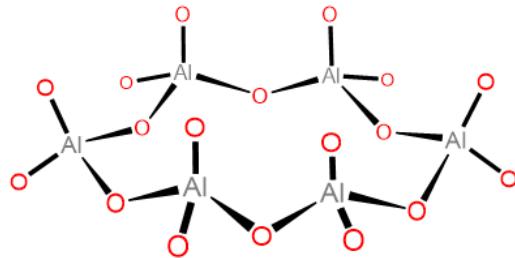
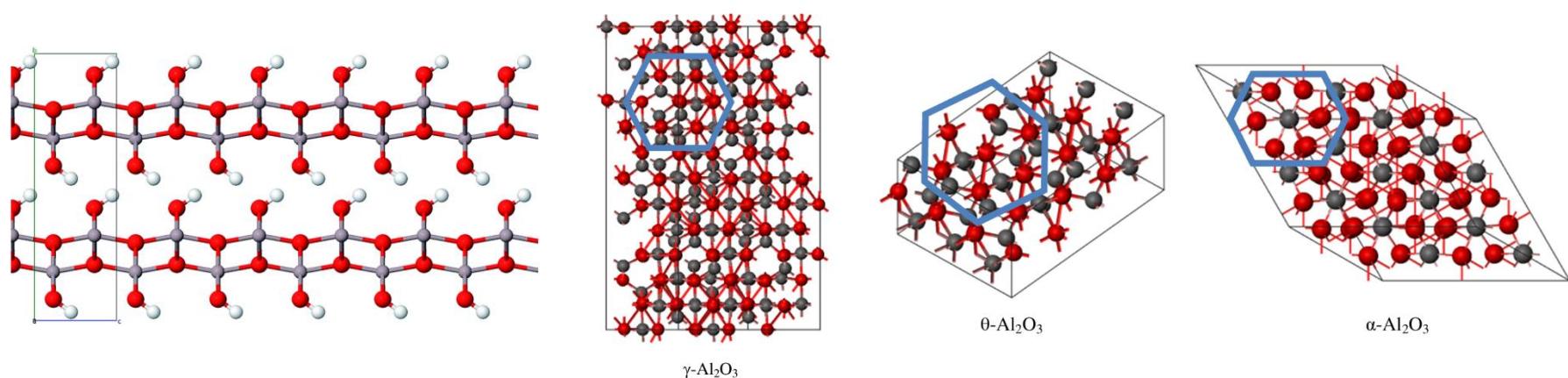
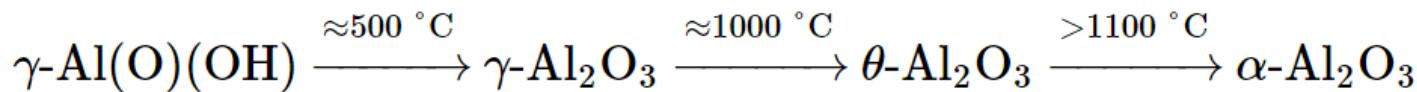


$$(\chi_A - \chi_B)^2 \propto q^2 \propto \Delta E$$

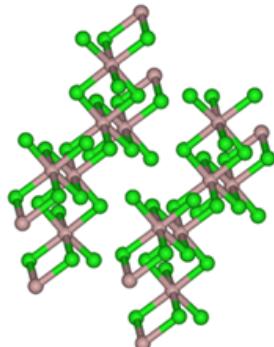
Reference points:  $X_F = 4.0$ ,  $X_H = 2.2$   
 $X_O = 3.4$ ,  $X_{AI} = 1.6$



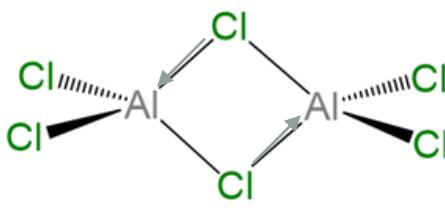
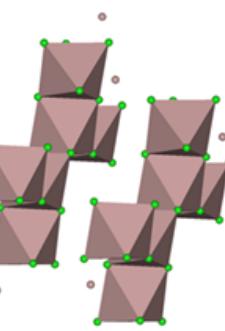
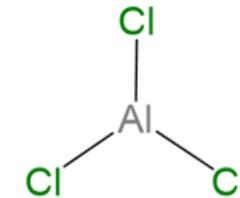
# $\text{Al}_2\text{O}_3$ , aluminum oxide or alumina



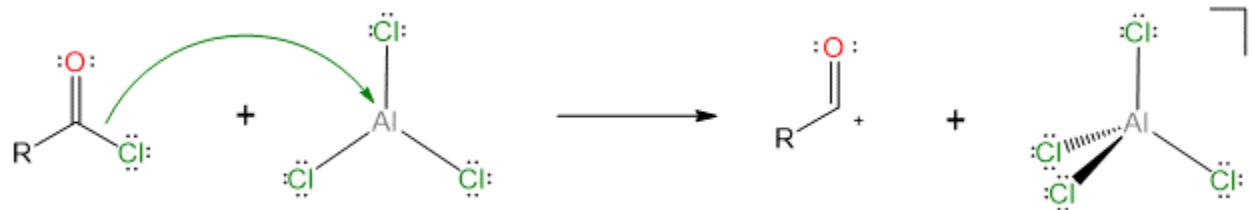
# $\text{AlCl}_3$ , aluminum trichloride



solid state crystal structure

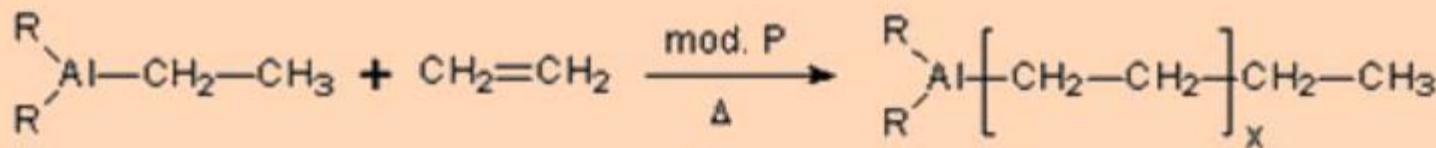
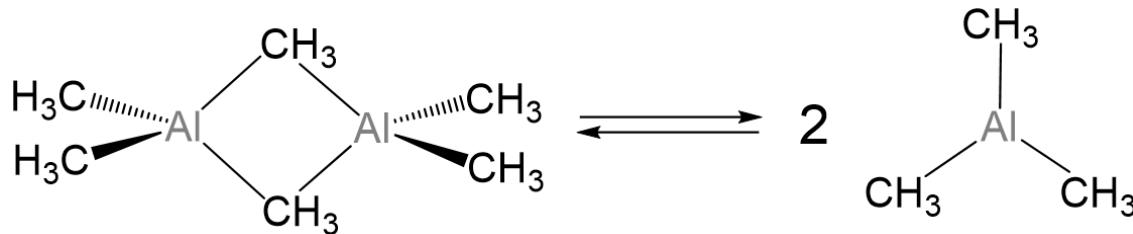
dimer  
(liquid and gas phases)monomer  
(high temperature gas phase)

The aluminum trihalides are effective Lewis acids, can be used as a catalyst in Friedel-Crafts alkylations and acylations.



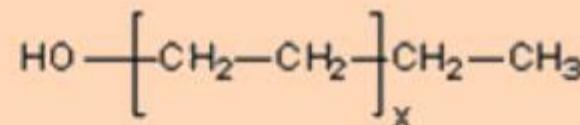
Group 13 trihalides tends to hydrolyze.

# Organometallic Compounds of Aluminium



↓  
oxidation

Ziegler Natta Polymerization  
Catalysts:  $\text{TiCl}_4/\text{AlEt}_3$



Oligomers with an even number of carbons

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# Orbital Energies of Transition Metals

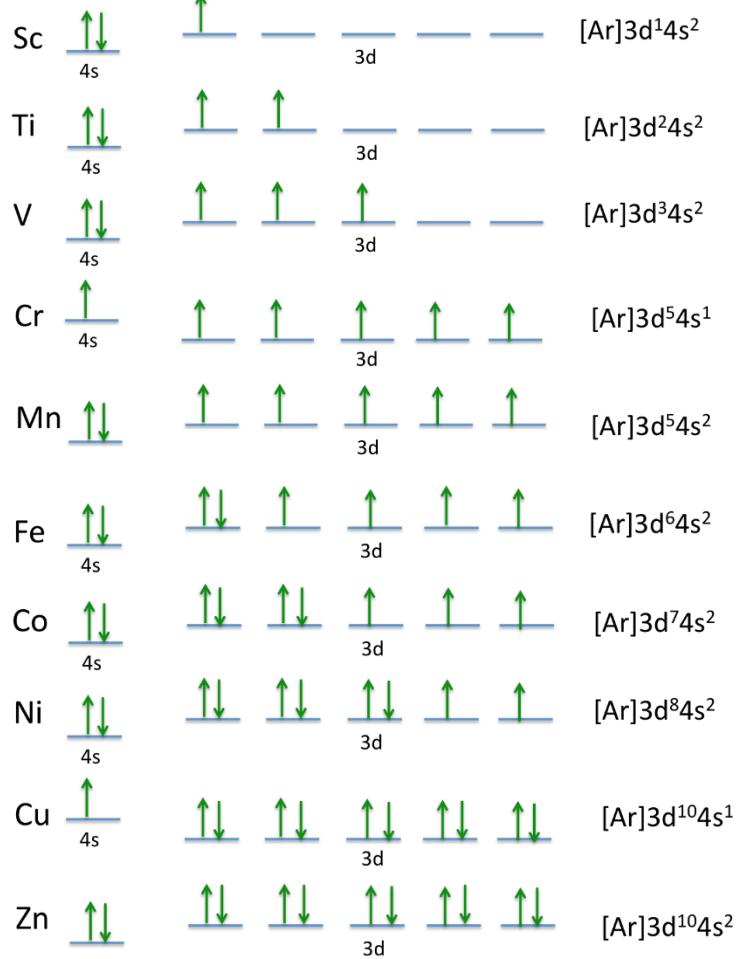
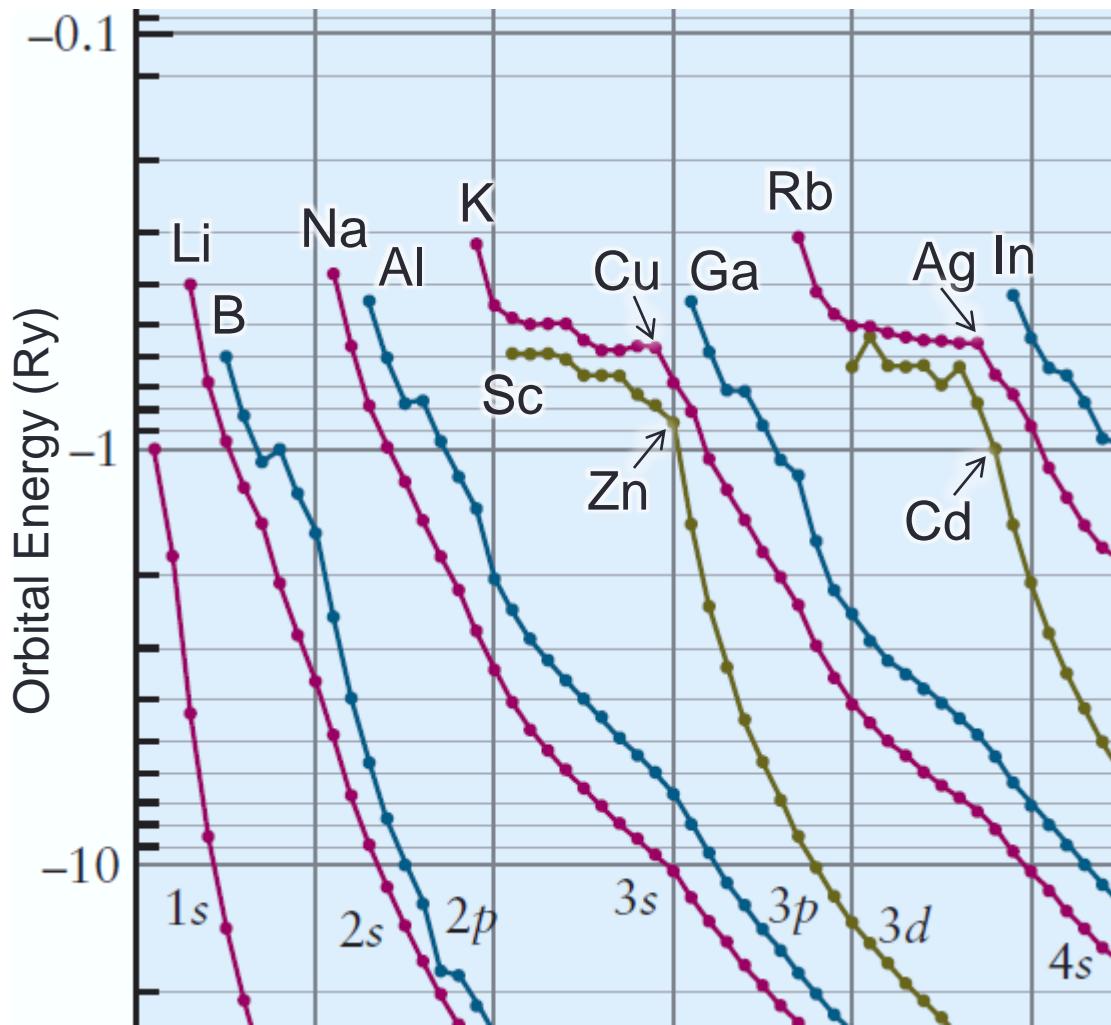


Fig. 5.26, OGB8 p.210



3	4	5	6	7	8	9	10	11	12
21 <b>Sc</b> [Ar]3d <sup>1</sup> 4s <sup>2</sup>	22 <b>Ti</b> [Ar]3d <sup>2</sup> 4s <sup>2</sup>	23 <b>V</b> [Ar]3d <sup>3</sup> 4s <sup>2</sup>	24 <b>Cr</b> [Ar] 3d <sup>5</sup> 4s <sup>1</sup>	25 <b>Mn</b> [Ar]3d <sup>5</sup> 4s <sup>2</sup>	26 <b>Fe</b> [Ar]3d <sup>6</sup> 4s <sup>2</sup>	27 <b>Co</b> [Ar]3d <sup>7</sup> 4s <sup>2</sup>	28 <b>Ni</b> [Ar]3d <sup>8</sup> 4s <sup>2</sup>	29 <b>Cu</b> [Ar]3d <sup>10</sup> 4s <sup>1</sup>	30 <b>Zn</b> [Ar]3d <sup>10</sup> 4s <sup>2</sup>
39 <b>Y</b> [Kr]4d <sup>1</sup> 5s <sup>2</sup>	40 <b>Zr</b> [Kr]4d <sup>2</sup> 5s <sup>2</sup>	41 <b>Nb</b> [Kr]4d <sup>3</sup> 5s <sup>2</sup>	42 <b>Mo</b> [Kr]4d <sup>5</sup> 5s <sup>1</sup>	43 <b>Tc</b> [Kr]4d <sup>5</sup> 5s <sup>2</sup>	44 <b>Ru</b> [Kr]4d <sup>7</sup> 5s <sup>1</sup>	45 <b>Rh</b> [Kr]4d <sup>8</sup> 5s <sup>1</sup>	46 <b>Pd</b> [Kr]4d <sup>10</sup>	47 <b>Ag</b> [Kr]4d <sup>10</sup> 5s <sup>1</sup>	48 <b>Cd</b> [Kr]4d <sup>10</sup> 5s <sup>2</sup>
57 <b>La</b> [Xe]6s <sup>2</sup> 5d <sup>1</sup>	72 <b>Hf</b> [Xe]5d <sup>2</sup> 6s <sup>2</sup>	73 <b>Ta</b> [Xe]5d <sup>3</sup> 6s <sup>2</sup>	74 <b>W</b> [Xe]5d <sup>4</sup> 6s <sup>2</sup>	75 <b>Re</b> [Xe]5d <sup>5</sup> 6s <sup>2</sup>	76 <b>Os</b> [Xe]5d <sup>6</sup> 6s <sup>2</sup>	77 <b>Ir</b> [Xe]5d <sup>7</sup> 6s <sup>2</sup>	78 <b>Pt</b> [Xe]5d <sup>9</sup> 6s <sup>1</sup>	79 <b>Au</b> [Xe]5d <sup>10</sup> 6s <sup>1</sup>	80 <b>Hg</b> [Xe]5d <sup>10</sup> 6s <sup>2</sup>

1st series                            2nd series                            3rd series

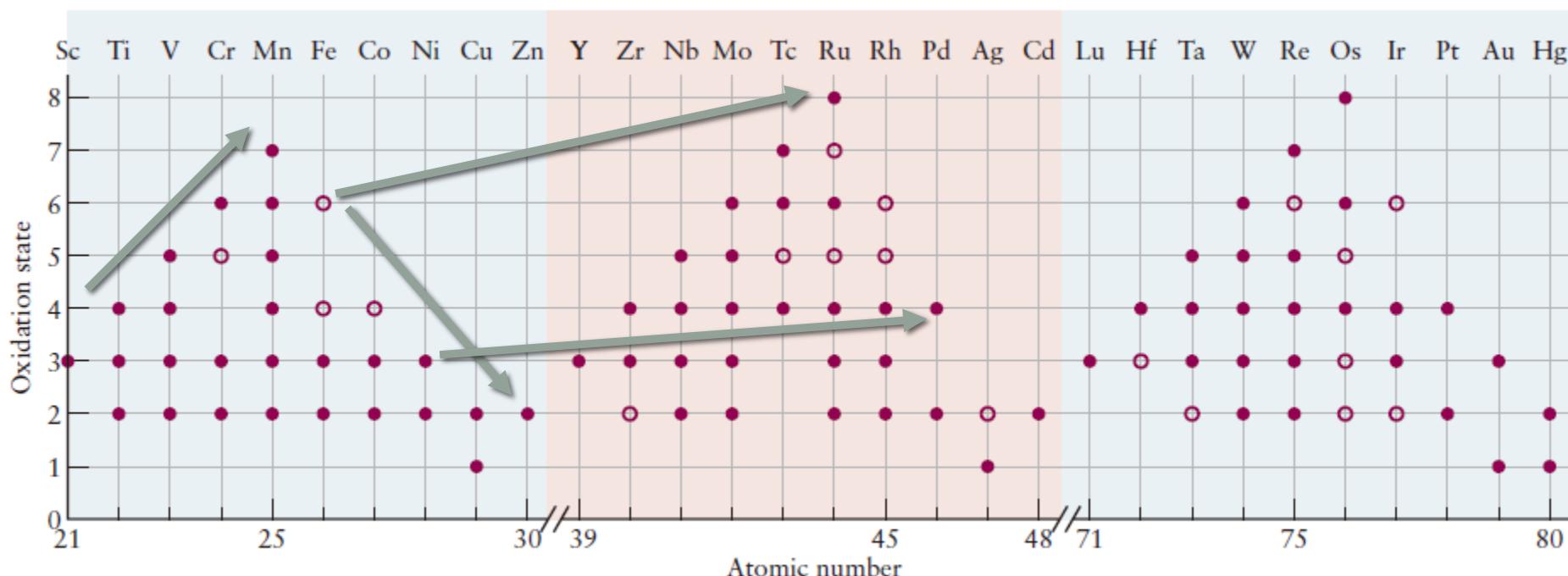
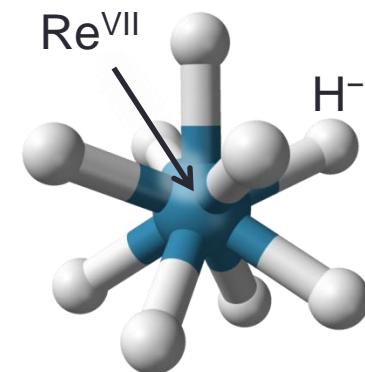


FIGURE 8.4 Some of the oxidation states found in compounds of the transition-metal elements. The more common oxidation states are represented by solid circles, and the less common ones are represented by open circles.

# Oxidation States of Transition Metals

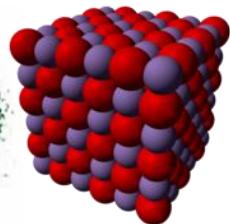
- Higher oxidation states are preferred in 5<sup>th</sup> / 6<sup>th</sup> periods



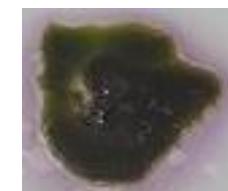
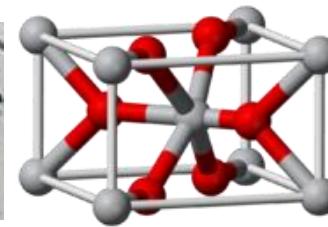
- Higher oxidation states lead to more covalent bonds



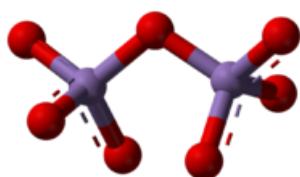
MnO



MnO<sub>2</sub>

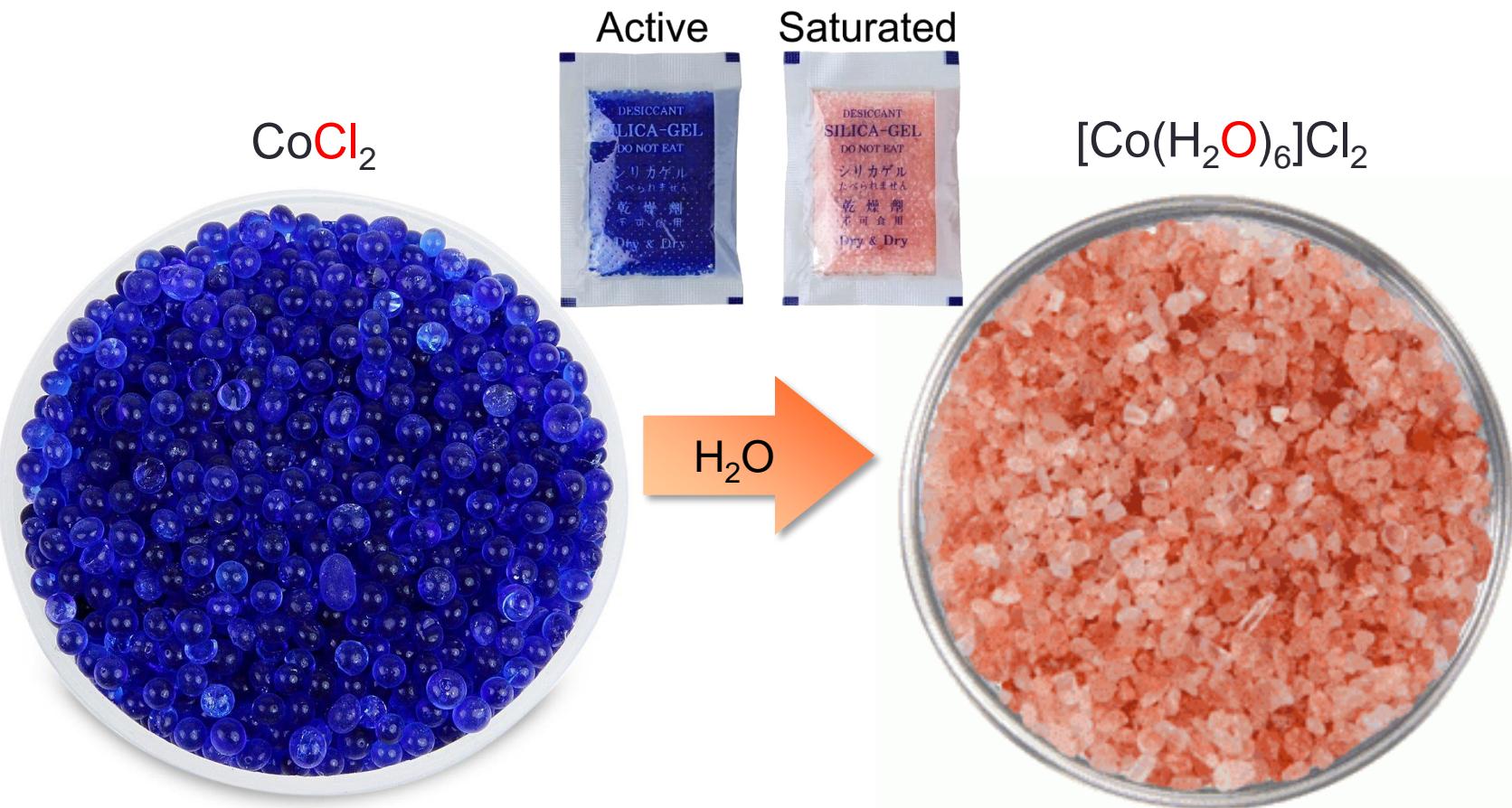


Mn<sub>2</sub>O<sub>7</sub>



# Colorful Transition Metal Ions

Indicating silica gel 变色硅胶



# Colorful Transition Metal Ions (2)



Corundum  
刚玉



Ruby  
红宝石



Sapphire  
蓝宝石



# Colorful Transition Metal Ions (3)



Emerald 祖母绿  
 $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Cr}^{3+}$

Yellow beryl 黄色绿宝石  
 $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}:\text{Fe}^{3+}$

Beryl 绿柱石/绿宝石  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$

# Colorful Transition Metal Ions (4)

Dr. and Mrs. R. Webster      168263      N. H. Stavisky  
G8582      176202

ALEXANDER SAPPHIRIOUS  
©老猫\_物种日历  
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**Grossular**  
Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>  
30 carats  
Ratnapura, Sri Lanka

**钙铝榴石**

**Grossular**  
Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>  
16.86 (total weight) and 15.93 carats  
Kenya/Tanzania

Mr. and Mrs. B. J. Whittle,  
Gemstone International      G10068      H. D. Haag  
G7918      Tiffany & Co. Foundation  
G10525

## Grossular Gemstones by Colour

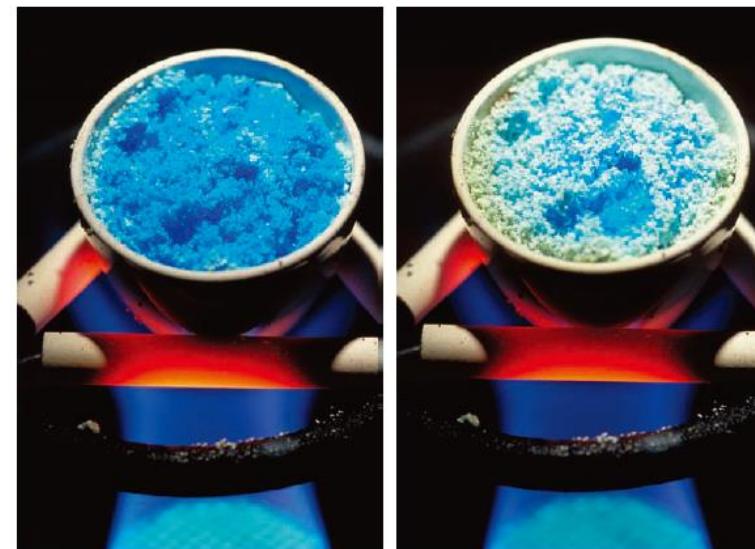
This table shows the variety of hues this gemstone can be found in. Click on a photo for more information.


# Introduction to Coordination Chemistry

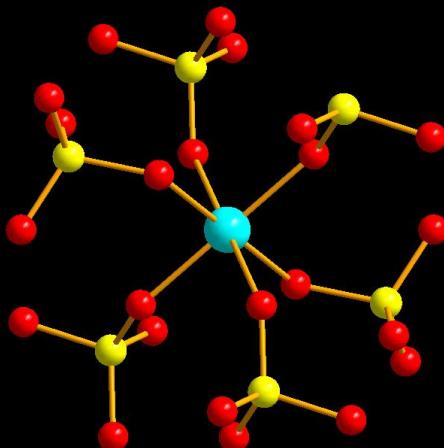
Coordination compounds 配位化合物, complex compounds 配合化合物, or sometimes simply complexes 配合物

contain bonds between a transition metal ion and one or more ligands. In forming these coordinate covalent bonds, the metal ions accept electron pairs from ligands.

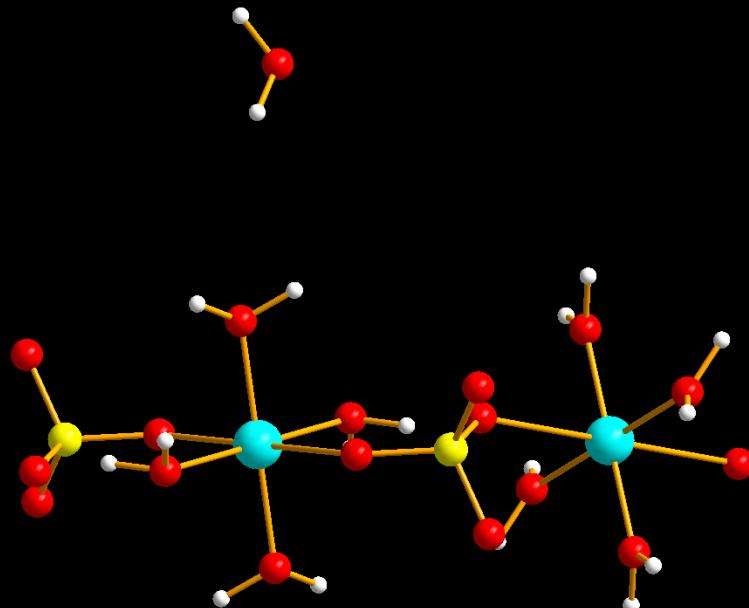
- $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
- $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$
- $[\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$
- $\text{K}_3[\text{Fe}(\text{CN})_6]$
- $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$



# Introduction to Coordination Chemistry

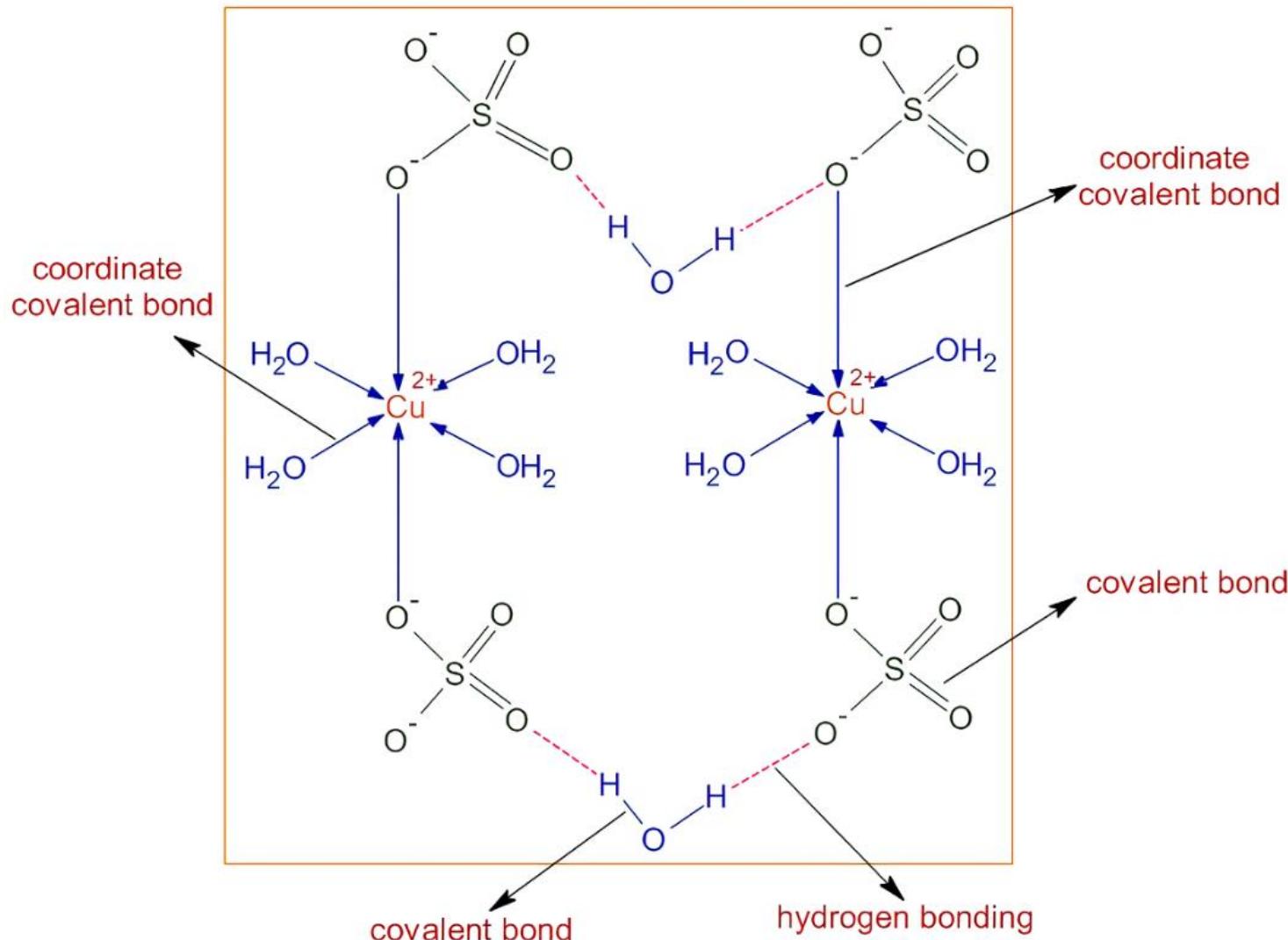


$\text{CuSO}_4$  (anhydrous)



$[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$

# Introduction to Coordination Chemistry



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# Surface Coordination Chemistry of Metal Nanomaterials

Pengxin Liu, Ruixuan Qin, Gang Fu\*, and Nanfeng Zheng\* [View Author Information ▾](#)

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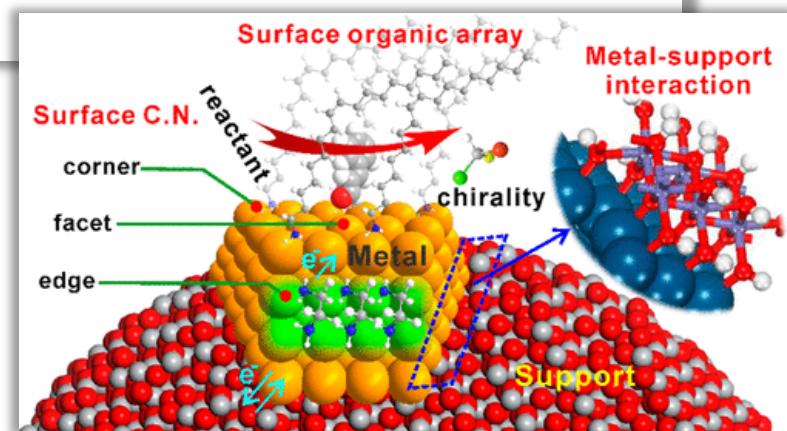
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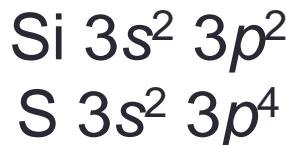
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-  Mendeley (350)

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**SUBJECTS:** Catalysts, Ligands, Metal nanoparticles, Metals, Palladium



# The 18-Electron Rule (1921)



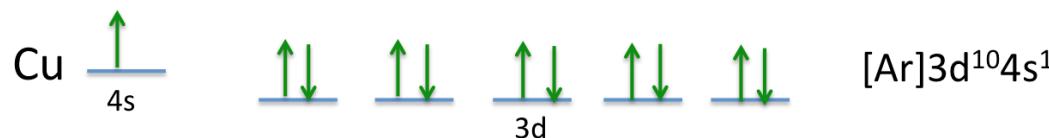
Octet rule



18-electron rule

# The 18-Electron Rule

- Early transition metals generally: electron count of 16 or less.
- Middle transition metals commonly have 18 electron count
- Late transition metals generally have 16 or lower electron count.
- When a structure has less than an 18 electron count, it is considered electron-deficient or coordinately unsaturated. This means that the compound has empty valence orbitals, making it electrophilic and extremely reactive.
- $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$



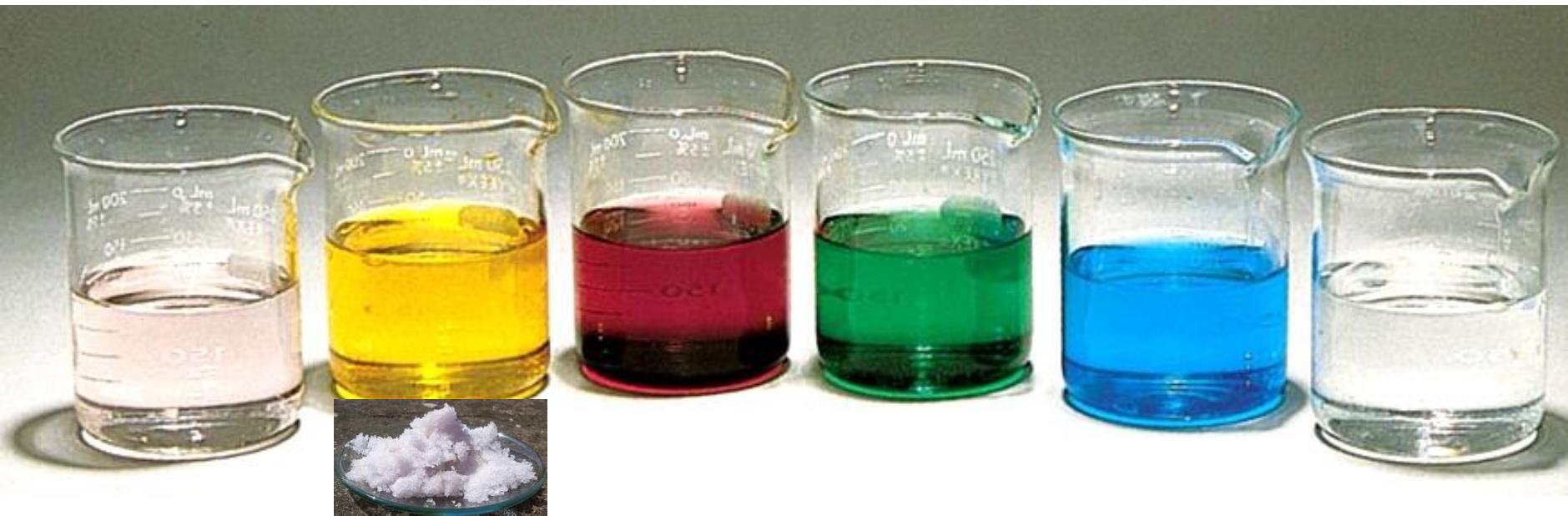
$\text{Cu}^{2+}: 9$   
 $4\text{H}_2\text{O}: 2 \times 4 = 8$   
Total: 17

# Electron counting

- Determine the oxidation state and the resulting **d-electron count**.
  - Identify if there are any overall charges on the molecular complex.
  - Identify the charge of each ligand.
- Determine the number of electrons from **ligand contribution**.
- Add up the electron counts for the metal and for each ligand.

Neutral 2e donors	Anionic 2e donors	Anionic 4e donors	Anionic 6e donors
H <sub>2</sub> O	X <sup>-</sup> (halide)	C <sub>3</sub> H <sub>5</sub> <sup>-</sup> (allyl)	Cp <sup>-</sup> (cyclopentadienyl)
NH <sub>3</sub> , NR <sub>3</sub>	OH <sup>-</sup>	O <sup>2-</sup> (oxide, double bond)	O <sup>2-</sup> (oxide, triple bond)
PH <sub>3</sub> , PR <sub>3</sub> (phosphines)	CH <sub>3</sub> <sup>-</sup> (methyl)	S <sup>2-</sup> (sulfide)	
CO (carbonyl)	CN <sup>-</sup>	NR <sup>2-</sup> (imide)	
alkenes	CR <sub>3</sub> <sup>-</sup> (alkyl)	CR <sub>2</sub> <sup>2-</sup> (alkylidene)	
alkynes	Ph <sup>-</sup> (phenyl)	OR <sup>-</sup> (alkoxide, bridging ligand)	
nitriles	H <sup>-</sup> (hydride)	SR <sup>-</sup> (thiolate, bridging ligand)	
	R <sub>n</sub> E <sup>-</sup> (silyl, germyl, alkoxo, amido etc.)	NR <sub>2</sub> <sup>-</sup> (inorganic amide, bridging ligand)	
		PR <sub>2</sub> <sup>-</sup> (phosphide, bridging ligand)	

# Hydrated Transition Metal Ions



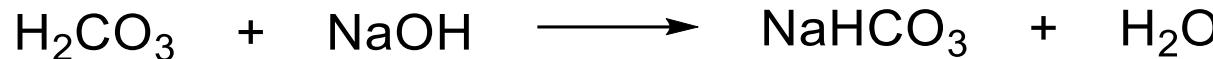
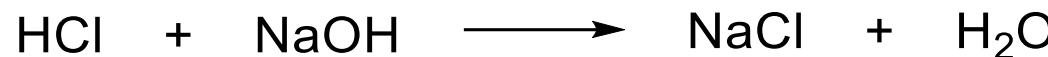
5	5	7	8	9	10
12	12	12	12	8	8
17	17	19	20	17	18

# Outline

- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
  - **Nature of coordination bonding: Lewis acid-base reaction**
  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - Coordination Theory
    - Crystal-field theory
    - Hybridization Valence Bond theory
    - Ligand-field theory
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

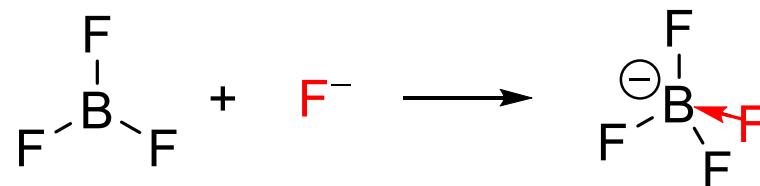
# Lewis acid / base

Brønsted–Lowry acid / base theory  
Protonic acid / base



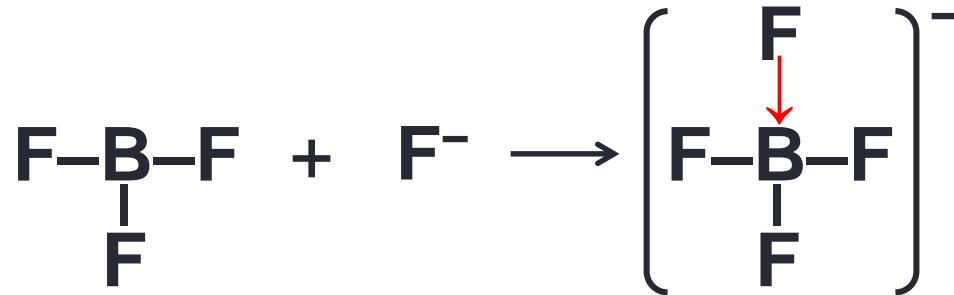
Acid      Base      Salt

Lewis acid / base



Acid      Base      Complex

# Lewis acid / base



Lewis  
Acid  
(e pair acceptor)

Lewis  
Base  
(donor)

Lewis  
adduct/complex  
加合物/配合物

# Hard and Soft Acids and Bases (1963)

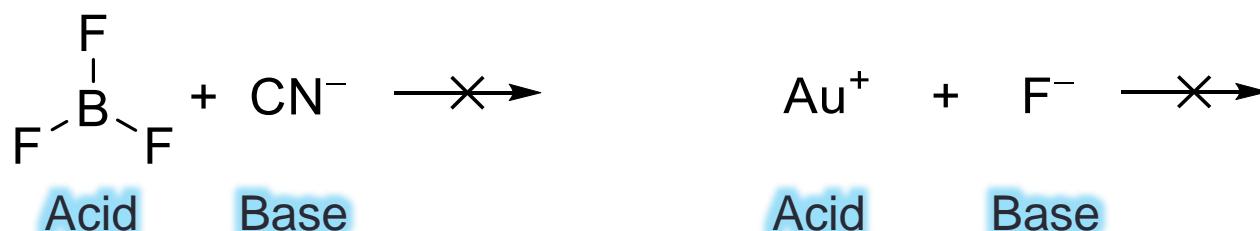


Ralph G. Pearson  
(Northwestern/  
UCSB, 1919–) (age 103)

Hard: Electron **tightly** bound  
Soft: Electron **loosely** bound



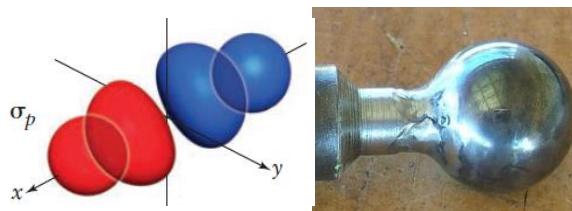
“硬亲硬,软亲软,软硬交界都不管”



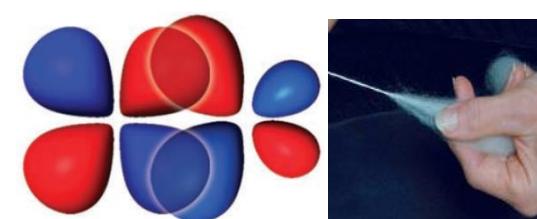
# HSAB (2)

Evaluation of hardness of HSAB

- Charge density: size, charge, electronegativity, orbital size
- Polarization



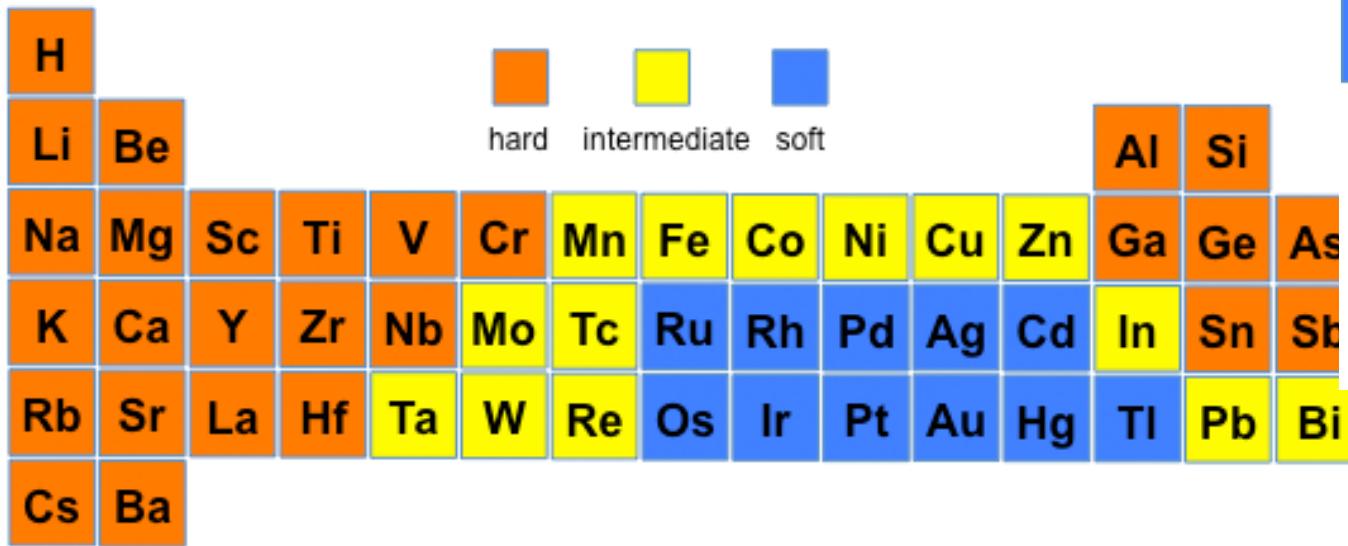
VS



## Classification of Lewis Acids and Bases<sup>†</sup>

	Hard	Borderline	Soft
<b>Acids</b>	$\text{H}^+$ , $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ $\text{Be}^{2+}$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ $\text{Cr}^{2+}$ , $\text{Cr}^{3+}$ , $\text{Al}^{3+}$ $\text{SO}_3$ , $\text{BF}_3$	$\text{Fe}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$ $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{Pb}^{2+}$ $\text{SO}_2$ , $\text{BBr}_3$	$\text{Cu}^+$ , $\text{Ag}^+$ , $\text{Au}^+$ , $\text{Tl}^+$ , $\text{Hg}^+$ $\text{Pd}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Pt}^{2+}$ , $\text{HG}^{2+}$ $\text{BH}_3$
<b>Bases</b>	$\text{F}^-$ , $\text{OH}^-$ , $\text{H}_2\text{O}$ , $\text{NH}_3$ $\text{CO}_3^{2-}$ , $\text{NO}_3^-$ , $\text{O}^{2-}$ $\text{SO}_4^{2-}$ , $\text{PO}_4^{3-}$ , $\text{ClO}_4^-$	$\text{NO}_2^-$ , $\text{SO}_3^{2-}$ , $\text{Br}^-$ $\text{N}_3^-$ , $\text{N}_2$ $\text{C}_6\text{H}_5\text{N}$ , $\text{SCN}^-$	$\text{H}^-$ , $\text{R}^-$ , $\text{CN}^-$ , $\text{CO}$ , $\text{I}^-$ $\text{CN}^-$ , $\text{R}_3\text{P}$ , $\text{C}_6\text{H}_6$ $\text{R}_2\text{S}$

# HSAB (3)



hard	intermediate	soft
C	N	O
F		
P	S	Cl
As	Se	Br
Sb	Te	I

Stability: HF > HCl > HBr > HI

Solubility:  $\text{AgF} \gg \text{AgCl} > \text{AgBr} > \text{AgI} \approx \text{AgCN} > \text{Ag}_2\text{S}$   
 $\text{CsF} > \text{NaF} \gg \text{LiF} > \text{CaF}_2$

Goldschmidt's rules in Geology: Li, Mg, Ca, Ti, Al, Ba, Fe  
vs. Cd, Ni, Ag, Cu, Zn, Hg

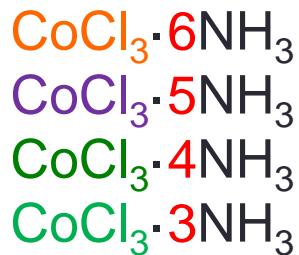
# Summary

- For transition metal, **d-orbitals** determine their chemistry
  - Lose **ns** and **(n-1)d** electron
  - Gain electron pair
- Coordination bond is not limited to TM
- For TM compound
  - **Lewis acid**: Central metal cation
  - **Lewis base**: Ligands
  - **Coordination compound**: Lewis adduct/complex
- HSAB

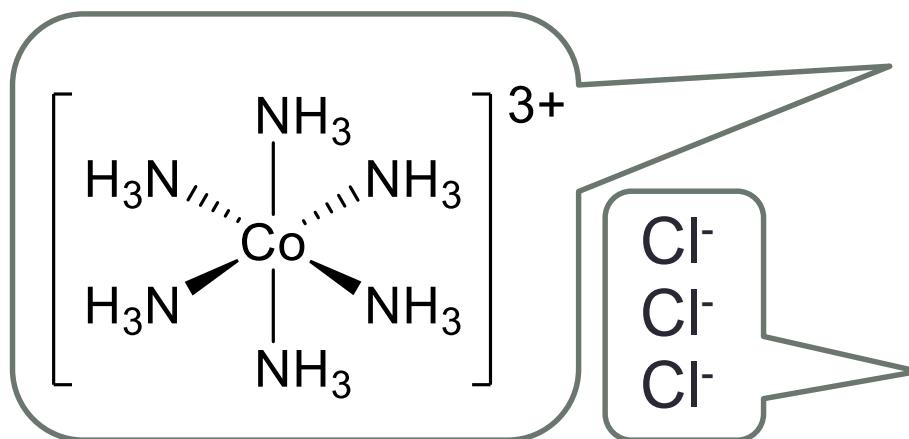
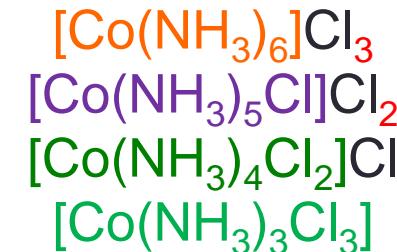
# Outline

- Metal
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    - Crystal-field theory
    - Hybridization Valence Bond theory
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    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

# Cobaltammines 钴氨化合物



HCl

NH<sub>3</sub> nonreactiveTitration of Cl<sup>-</sup> anions with AgNO<sub>3</sub>

Inner  
coordination  
sphere  
内界

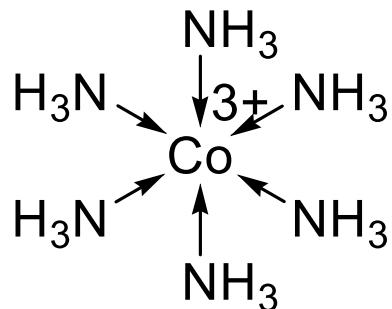
Outer  
coordination  
sphere  
外界

Hexaaminecobalt(III) chloride  
三氯化六氨合钴

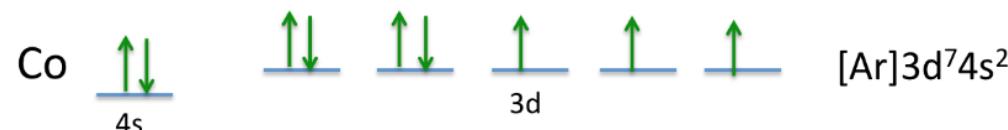


Alfred Werner  
(Zürich, 1866–1919)  
1913 Nobel Chemistry award

# Cobaltammines (2)

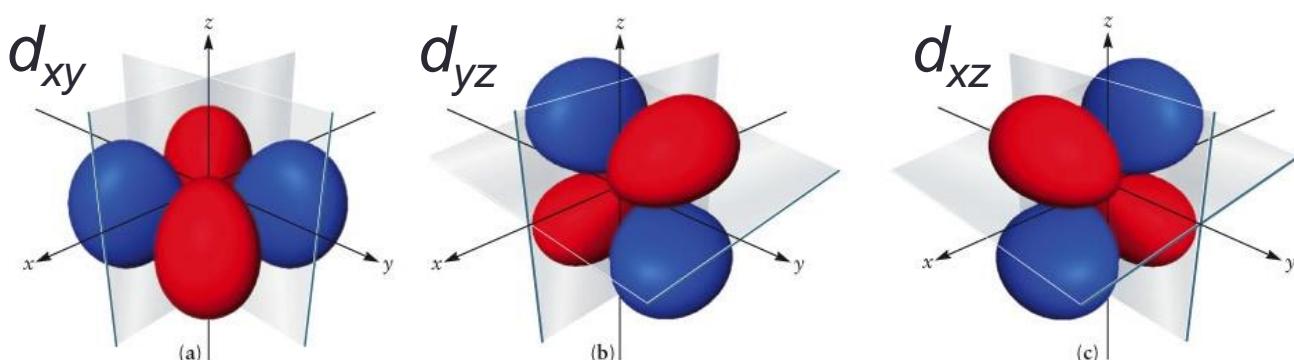
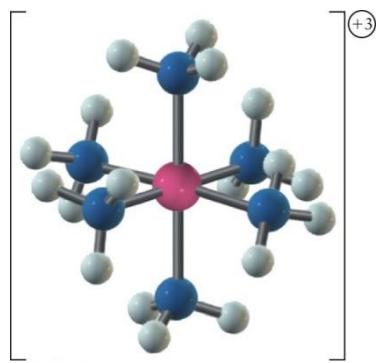


Octahedral coordination 八面体配位

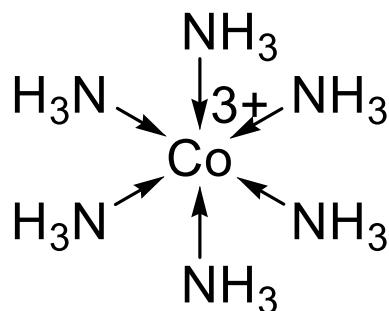


$$9 - 3 + 2 \times 6 = 18$$

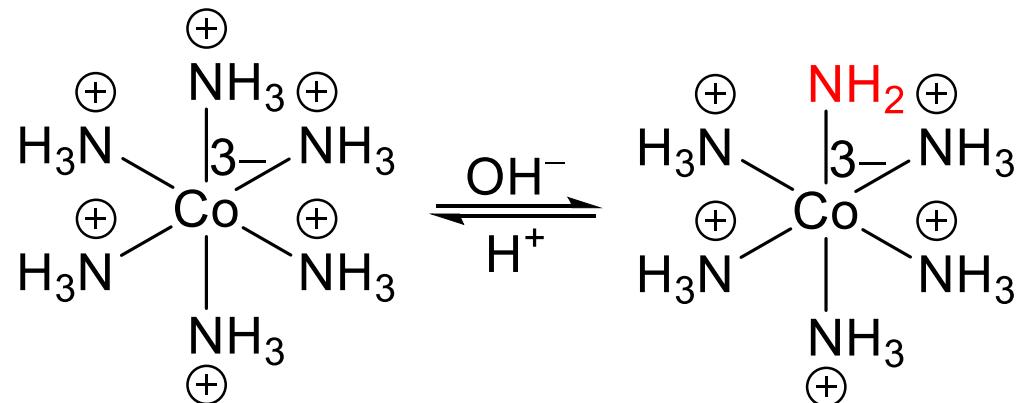
$18 \text{ e} = 6 \text{ Co-N bonds } (\sigma) + 3 \text{ lone pairs } (d \text{ or } \delta)$



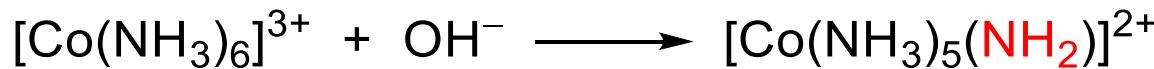
# Cobaltammines (3)



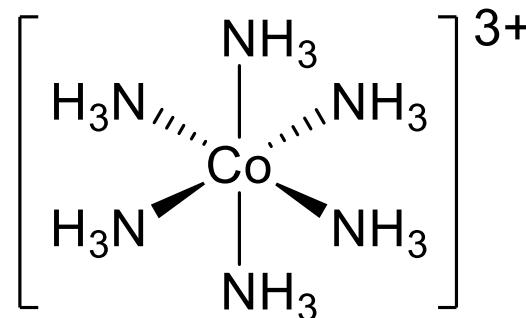
$$9 - 3 + 2 \times 6 = 18$$



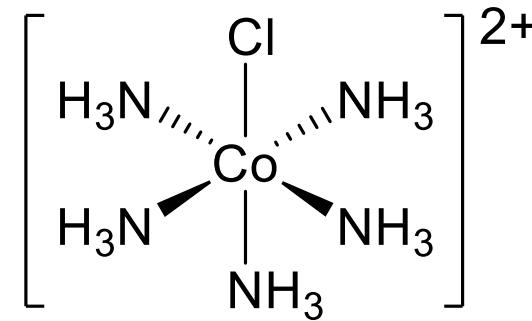
$$9 + 3 + 1 \times 6 = 18$$



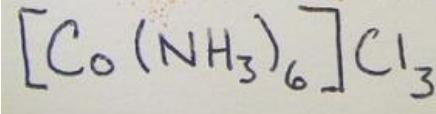
# Cobaltammines (4)



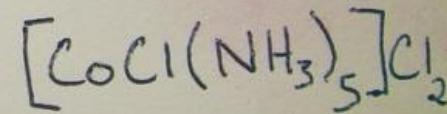
Hexaaminecobalt(III)  
六氨合钴(III)



Pentaaminechlorocobalt(III)  
一氯五氨合钴(III)

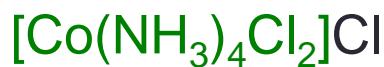
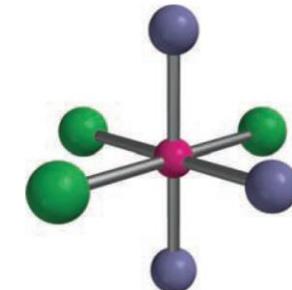
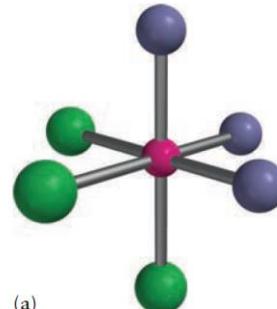
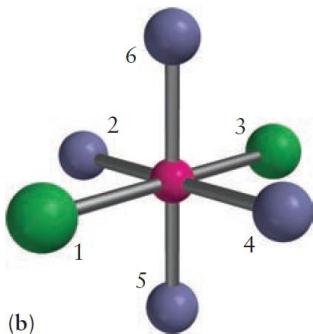
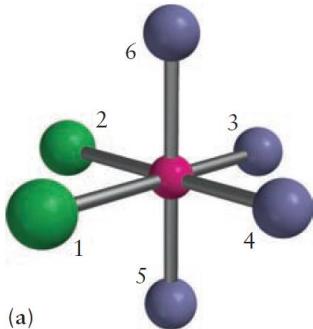


Hexaaminecobalt(III) chloride  
三氯化六氨合钴(III)



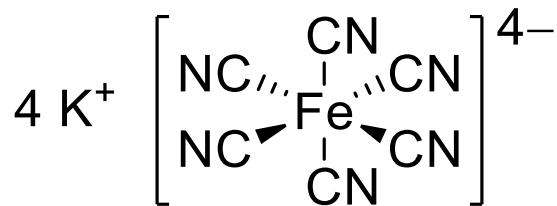
Pentaaminechlorocobalt(III) chloride  
二氯化一氯五氨合钴(III)

# Cobaltammines (5)



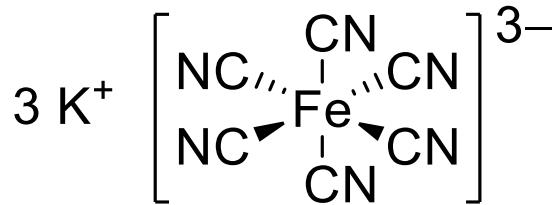
# Ferrocyanide and Ferricyanide (1)

草木灰和牛血



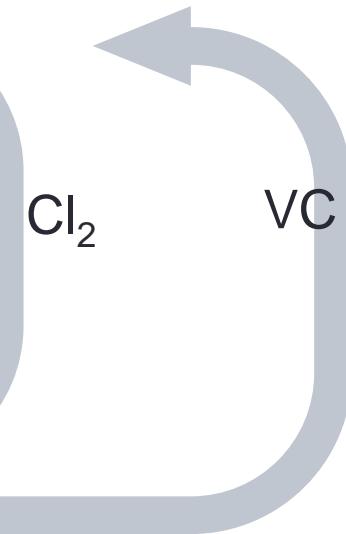
Potassium **ferrocyanide** 亚铁氰化钾, 黄血盐

Potassium hexacyano**ferrate(II)** 六氰合铁(II)酸钾

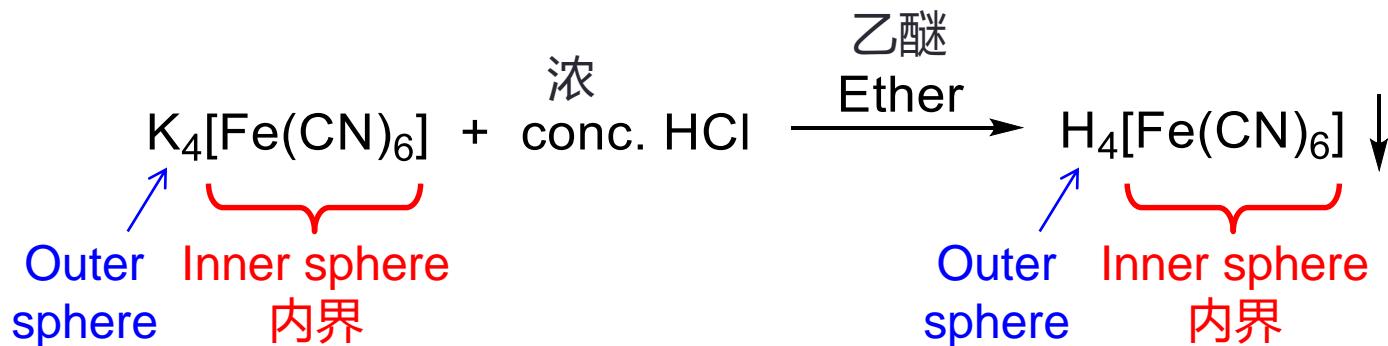
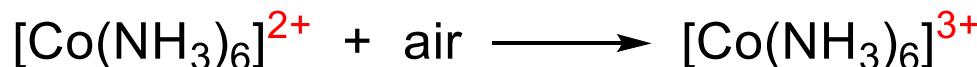
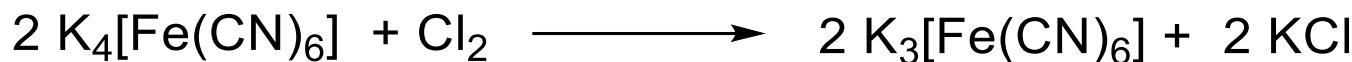


Potassium **ferricyanide** 铁氰化钾, 赤血盐

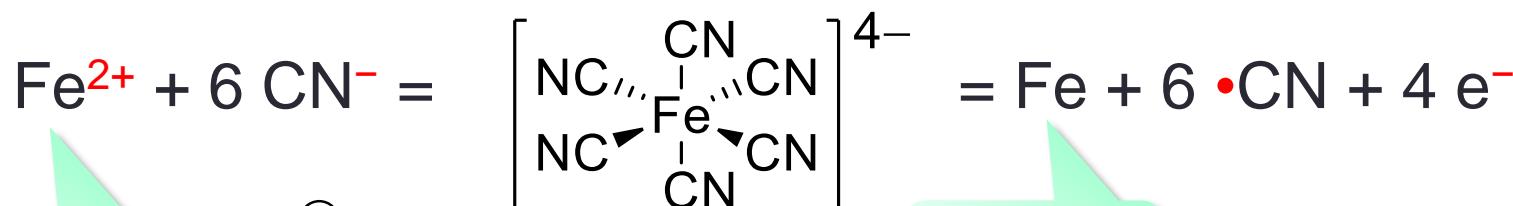
Potassium hexacyano**ferrate(III)** 六氰合铁(III)酸钾



# Ferrocyanide and Ferricyanide (2)



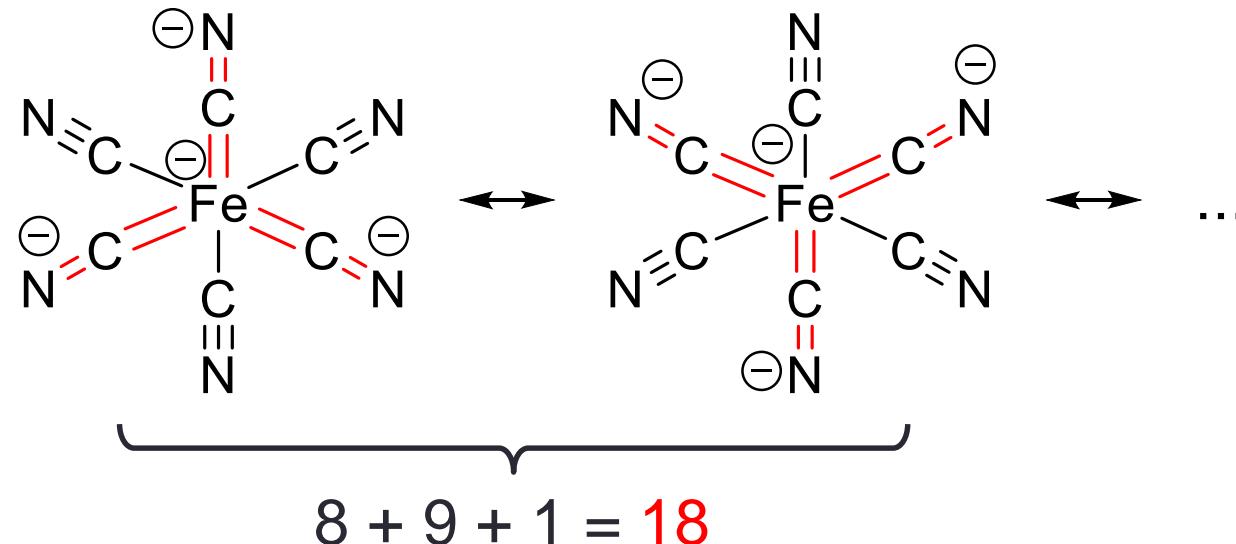
# Ferrocyanide and Ferricyanide (3)

 $3d^6$ 

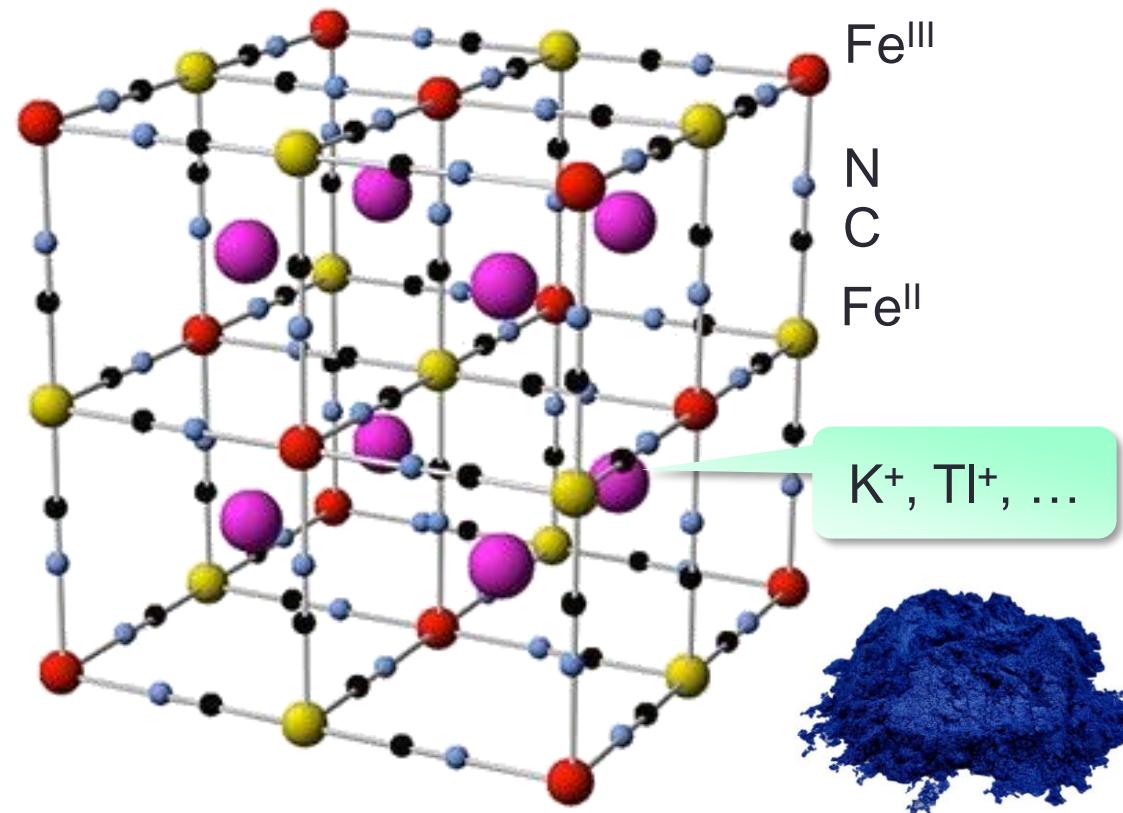
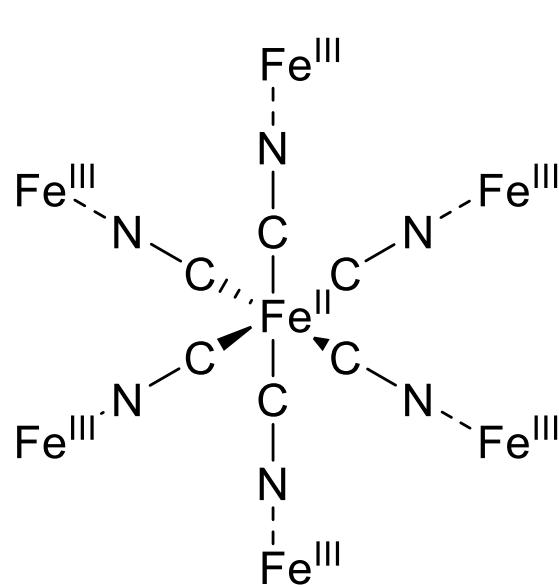
$$6 + 2 \times 6 = 18$$

 $3d^6 4s^2$ 

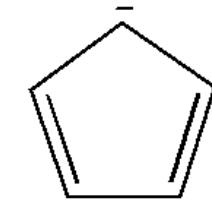
$$8 + 1 \times 6 + 4 = 18$$



# Ferrocyanide and Ferricyanide (4)



# Ferrocene 二茂铁



$\text{Fe}(\text{C}_5\text{H}_5)_2$   
M.p. 173°C, B.p. 249°C  
**Insoluble** in  $\text{H}_2\text{O}$ ,  
Soluble in  $\text{C}_6\text{H}_6$ ,  $\text{CH}_2\text{Cl}_2$

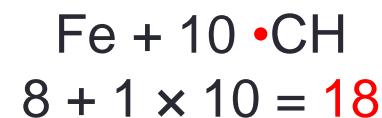
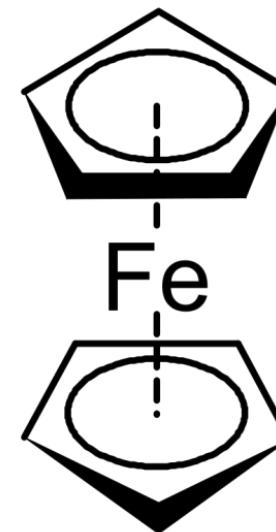
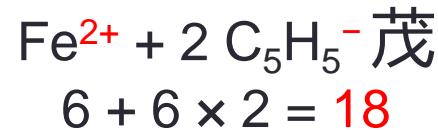
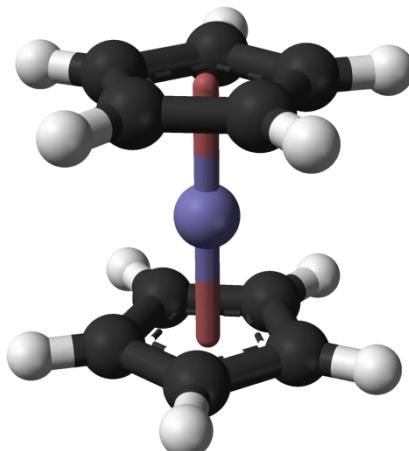


# Ferrocene (2)

3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd



Geoffrey Wilkinson  
(Imperial, 1921–1996)      Ernst Otto Fischer  
(Munich, 1918–2007)

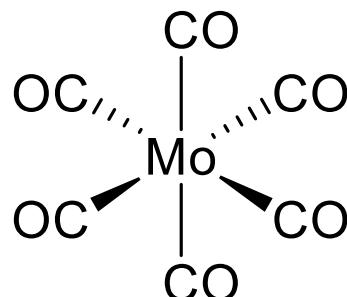


3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd

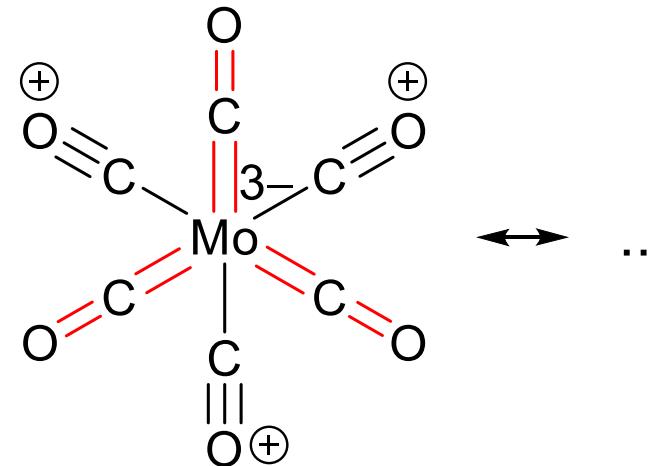
# Metal Carbonyls (1)

Hexacarbonyl molybdenum(0)

六羰基合钼(0)

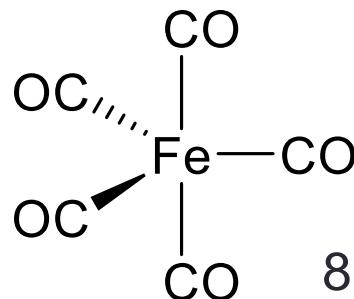


$$6 + 2 \times 6 = 18$$



Pentacarbonyl iron(0)

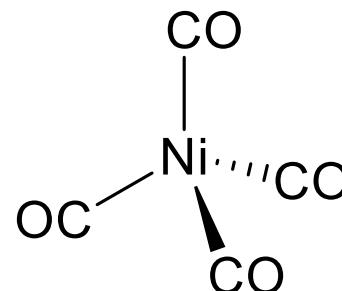
五羰基合铁(0)



$$8 + 2 \times 5 = 18$$

Tetracarbonyl nickel(0)

四羰基合镍(0)

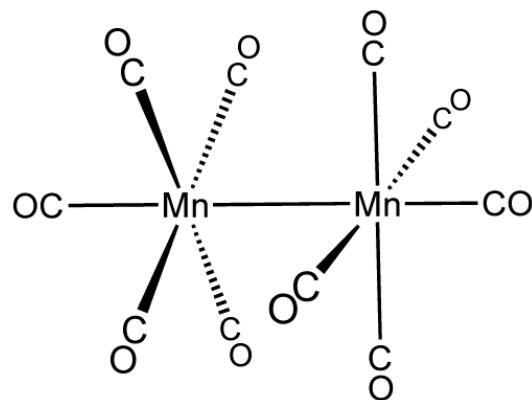


$$10 + 2 \times 4 = 18$$

3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd

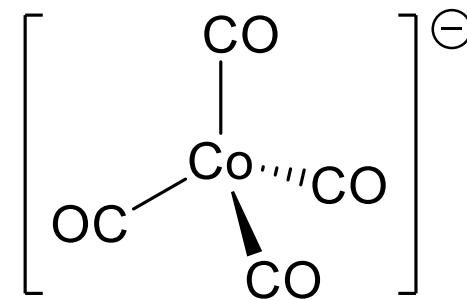
# Metal Carbonyls (2)

Bis[penta**carbonyl**manganese(0)]  
双[五羰基合锰(0)]



$$7 + 2 \times 5 + 1 = 18$$

Tetra**carbonyl**cobalt(-1)  
四羰基合钴(-1)



$$9 + 2 \times 4 + 1 = 18$$

# Metal Oxos (1)

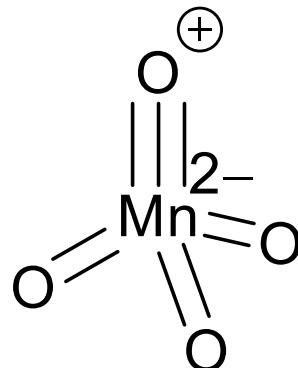
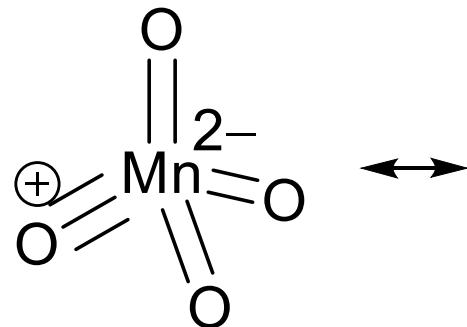
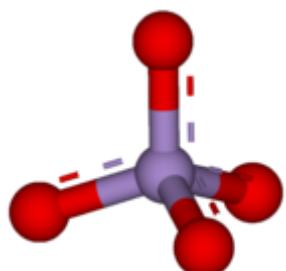
3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd



$\text{KMnO}_4$  高锰酸钾  
Potassium permanganate



$\text{K}_2\text{CrO}_4$  铬酸钾  
Potassium chromate



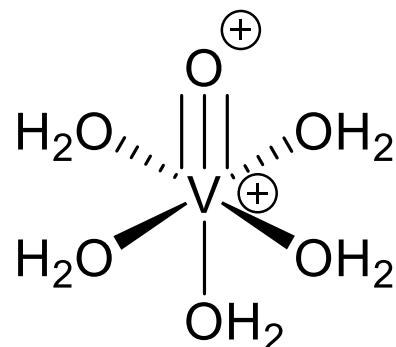
$$0 + 4 \times 3 + 6 = 18$$

or  $2 \times 9 = 18$

...

# Metal Oxos (2)

3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg



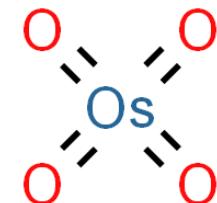
$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$   
 Vanadyl(IV) sulfate pentahydrate  
 五水合硫酸氧钒(IV)

$$1 + 2 \times 5 + 6 = 17$$

Or  $1 + 2 \times 8 = 17$



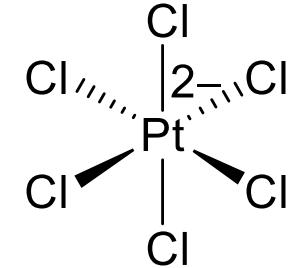
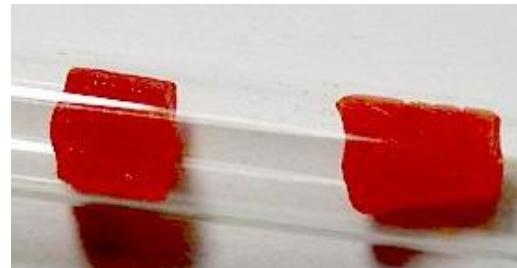
$\text{OsO}_4$   
 Osmium tetroxide  
 四氧化锇



3 4 5 6 7 8 9 10 11 12

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

# Platinum Group Compounds



Pt in aqua regia 王水

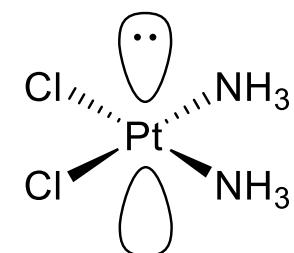
Chloroplatinic acid 氯铂酸  
 $\text{H}_2[\text{PtCl}_6]$

$$6 + 2 \times 6 = 18 \text{ or} \\ 10 + 1 \times 6 + 2 = 18$$



*cis*-diaminedichloroplatinum(II), cisplatin  
 顺二氯二氨合铂(II), 顺铂

$$8 + 2 \times 4 = 16 \\ 4 \sigma \text{ bonds} + 4 \text{ lone pairs}$$



# Summary

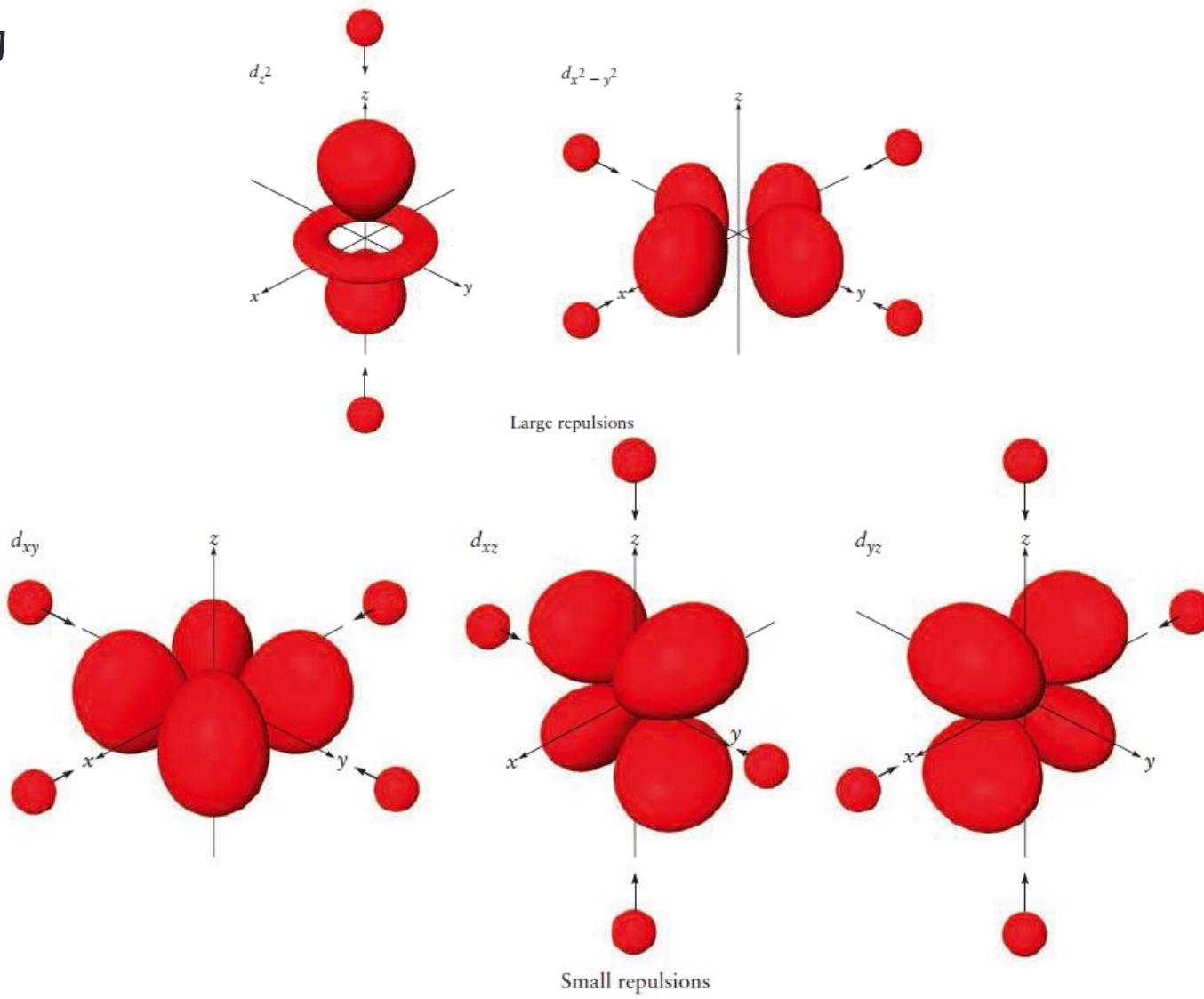
- Transition metals have *s*, *p*, *d* orbitals available for bonding
  - Can make 9 bonds with 18 valence electrons
- Multiple bonds between metal and ligand are common
  - $M=C$ ,  $M\equiv O$
  - Accounts for stability
- Transition-metal complexes appear in certain shapes
  - Octahedral
  - Tetrahedral
  - Square planar

# Outline

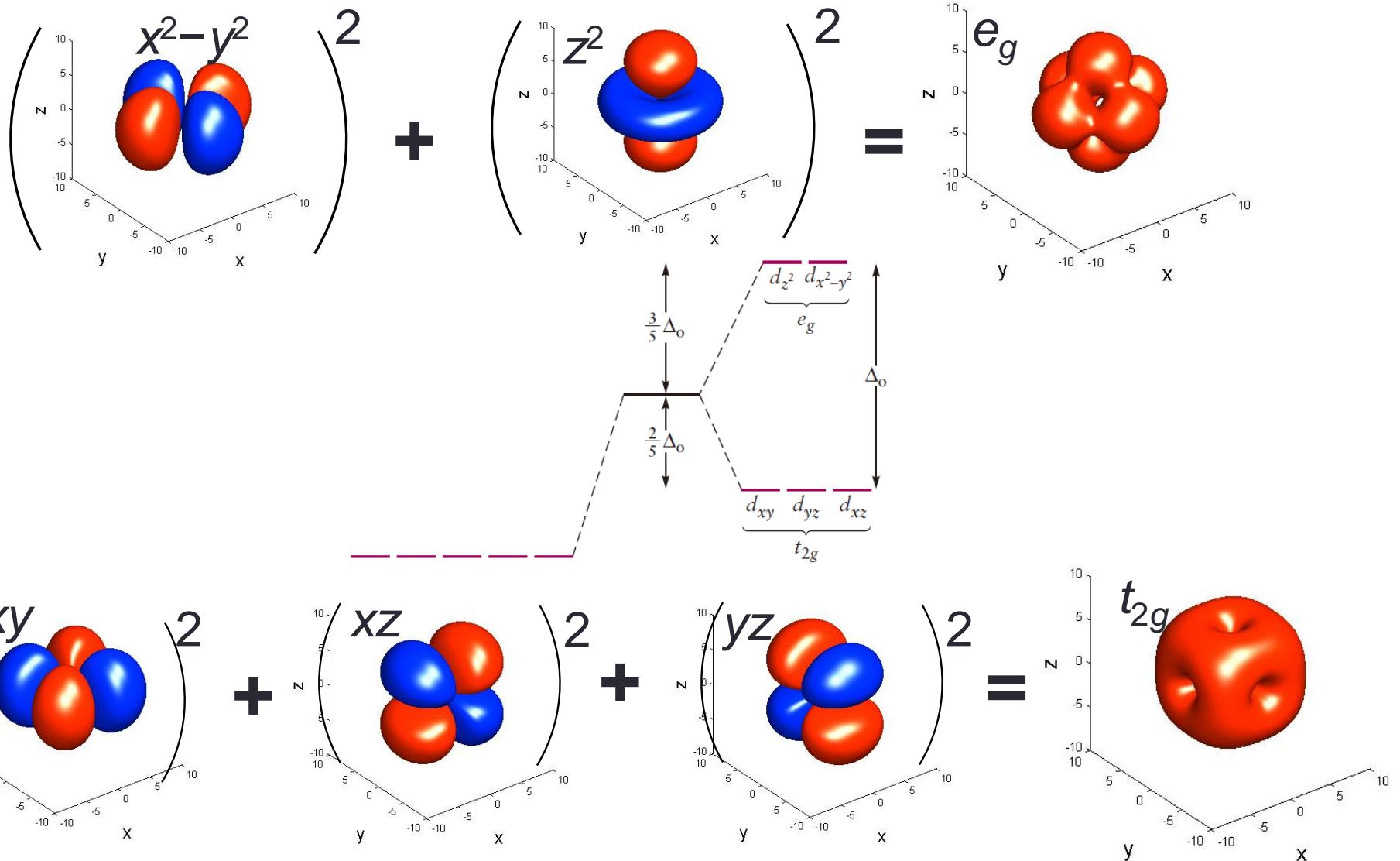
- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
  - Nature of coordination bonding: Lewis acid-base reaction
  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - Coordination Theory
    - Crystal-field theory
    - Hybridization Valence Bond theory
    - Ligand-field theory
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

# Crystal Field Theory based on ionic description

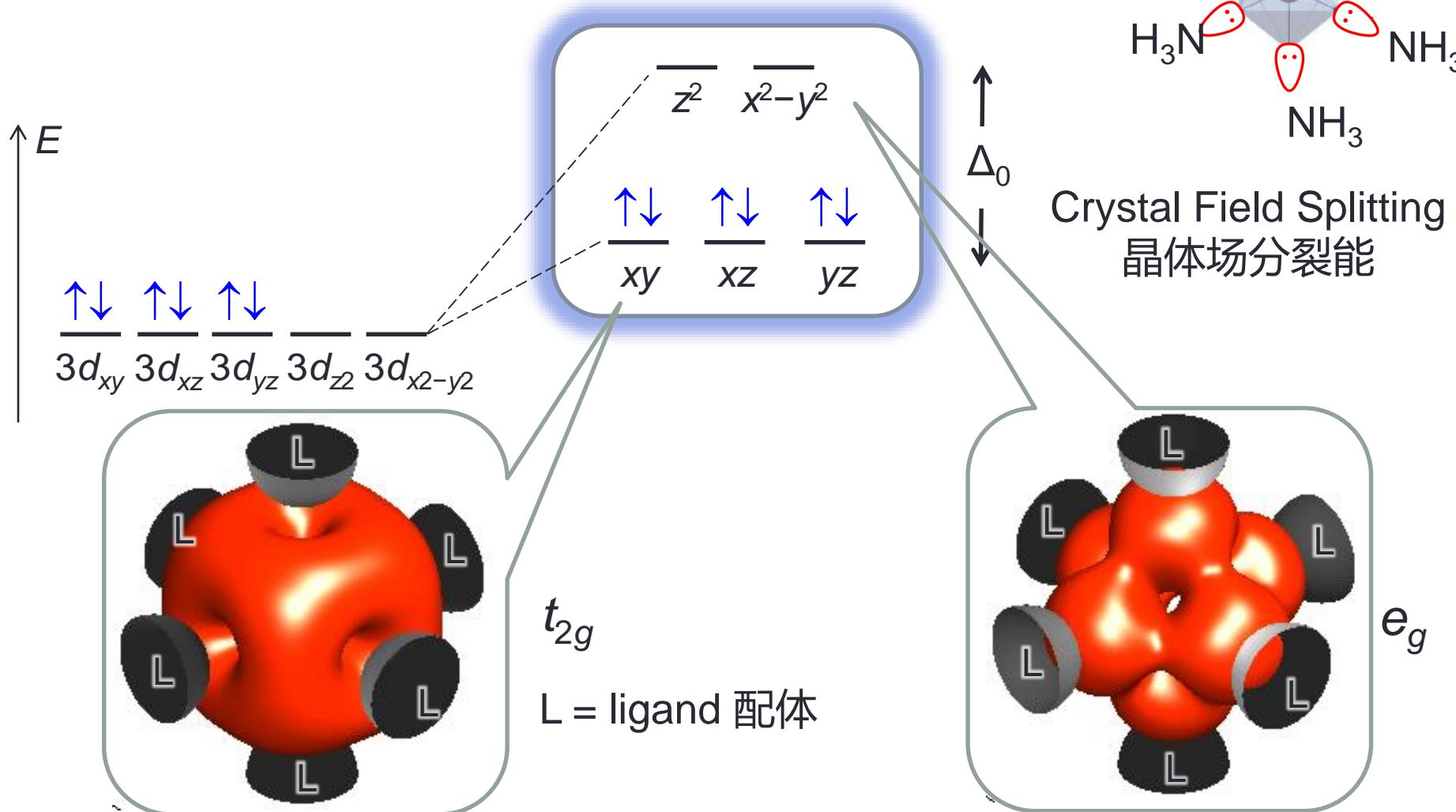
排斥力



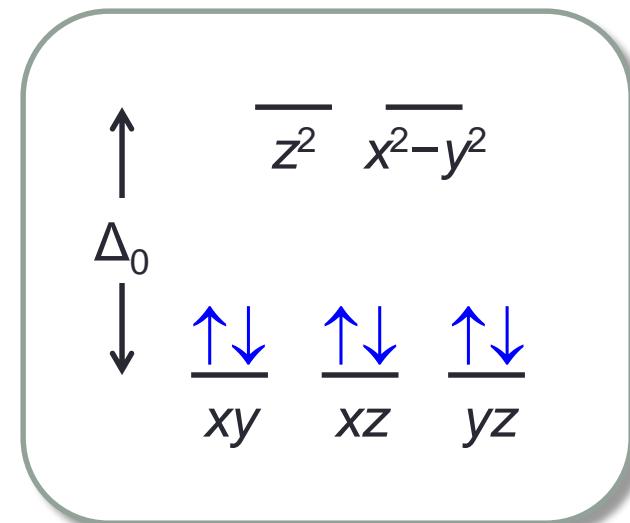
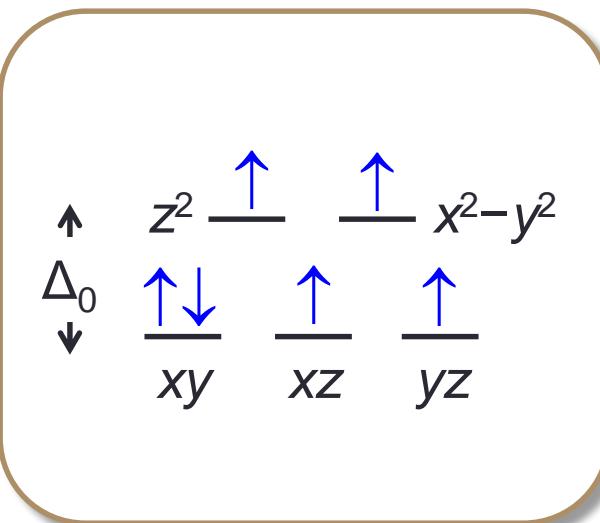
# Crystal Field Splitting



# Crystal Field Theory

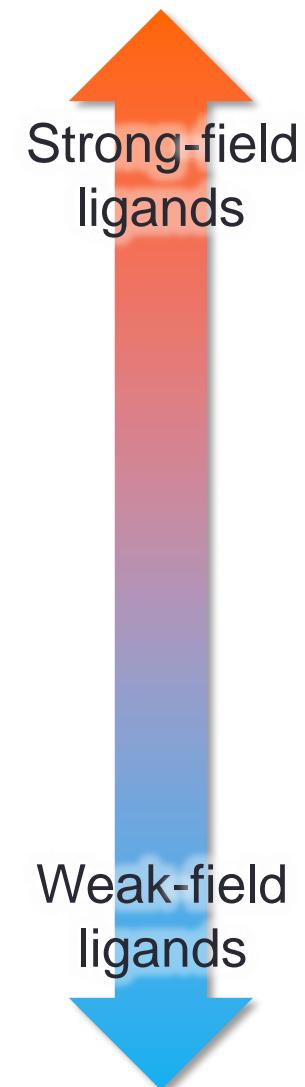
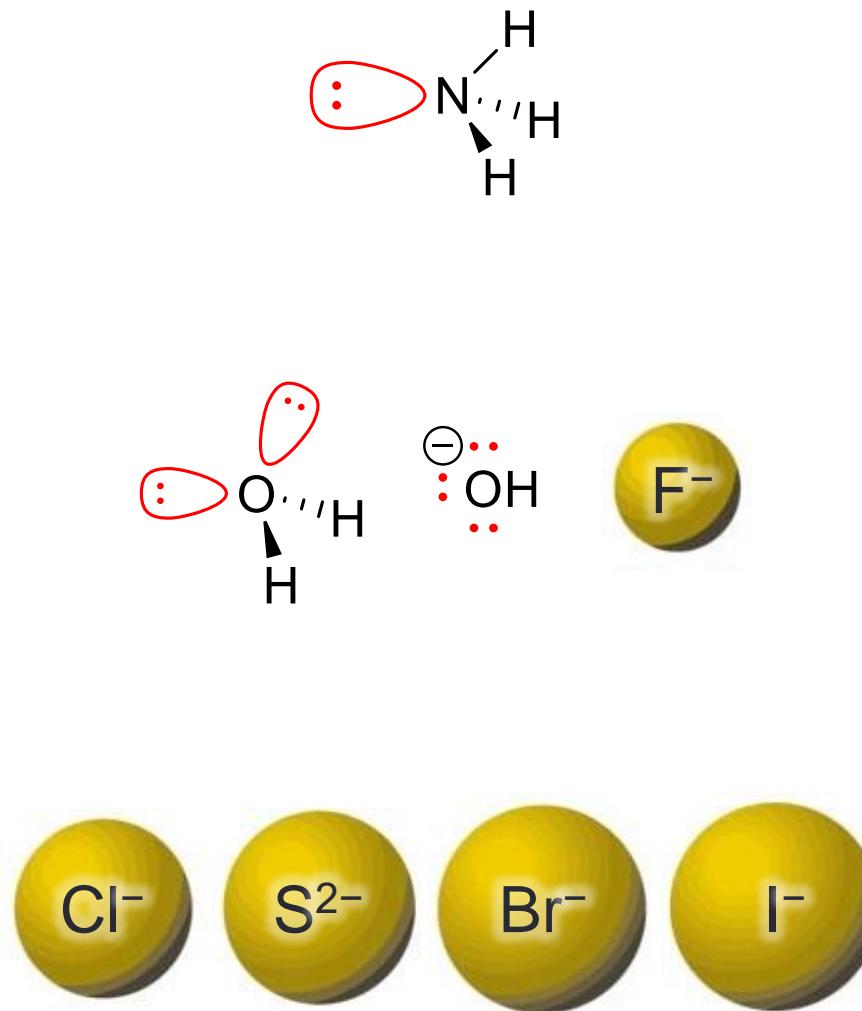
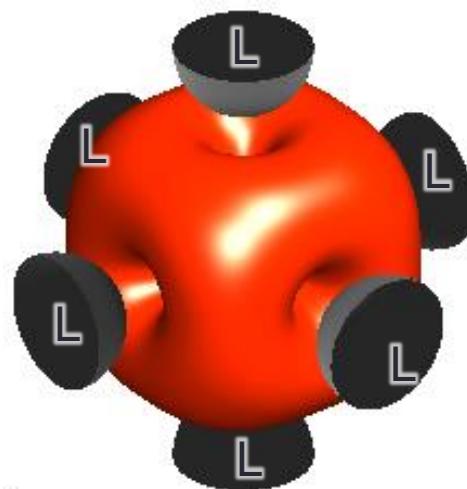
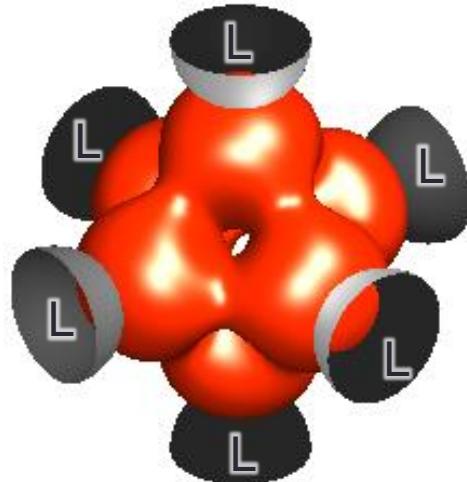


# Weak vs. Strong Field Ligands (1)

 $\text{CoF}_6^{3-}$  $\text{Co}(\text{NH}_3)_6^{3+}$ 

$\Delta_0$	1.80 eV	2.84 eV
spin	high	low
Color	Blue, absorbs at 690 nm	Orange, absorbs at 437 nm
18e rule	Does not apply	Applies
Chemistry	Less stable	Stable

# Weak vs. Strong Field Ligands (2)



# Ligands affect the electron configuration

- Rules of thumb:
- 3d complexes are **high spin** with **weak field** ligands, **low spin** with **strong field** ligands.
- High valent 3d complexes (e.g.,  $\text{Co}^{3+}$  complexes) tend to be **low spin** (large  $\Delta_o$ )
- 4d and 5d complexes are always **low spin** (large  $\Delta_o$ )

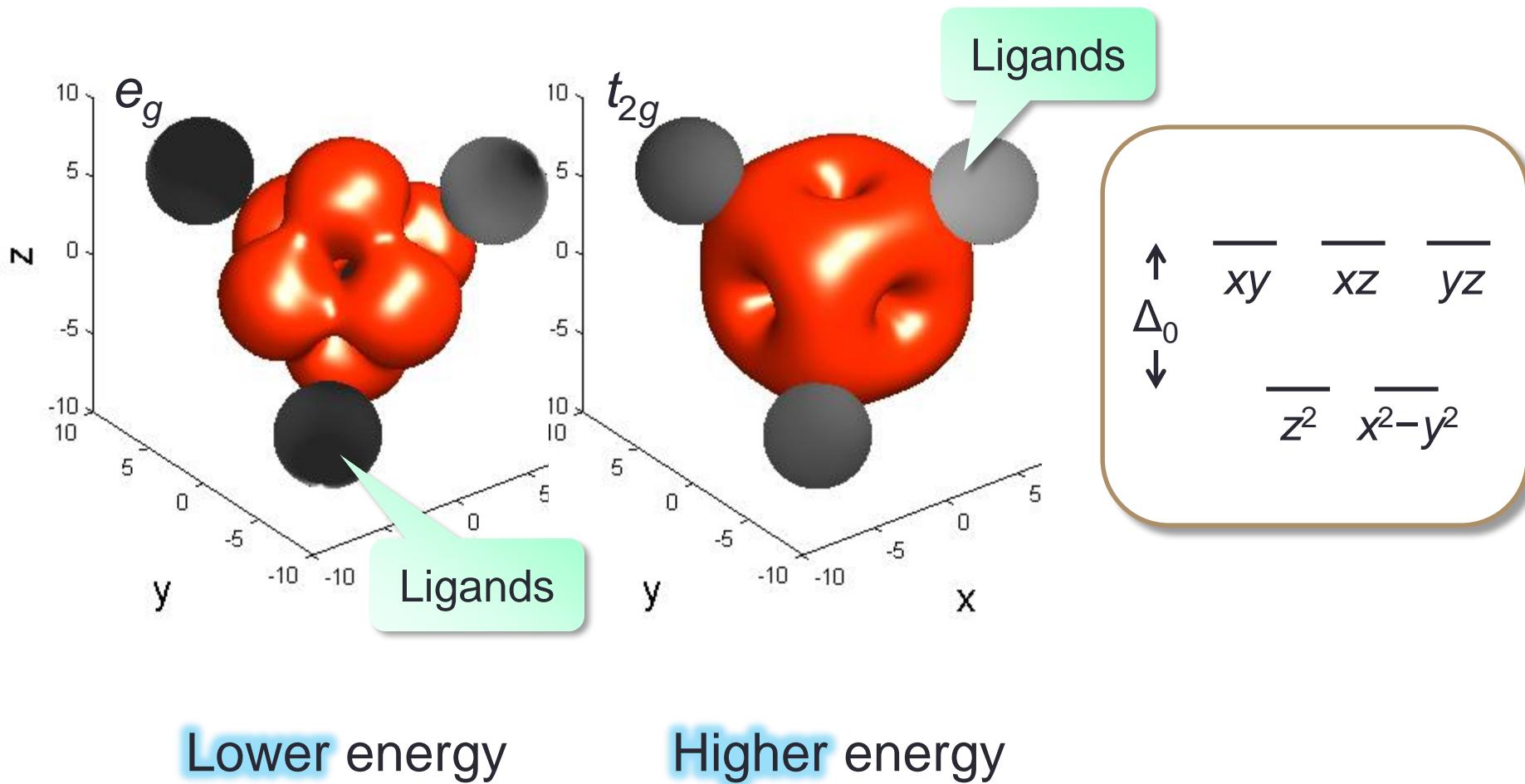
TABLE 8.5

Electron Configurations and Crystal Field Stabilization Energies for High- and Low-Spin Octahedral Complexes

Configuration		$d^1$	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$	$d^9$	$d^{10}$
Examples		$\text{Ti}^{3+}$	$\text{Ti}^{2+}, \text{V}^{3+}$	$\text{V}^{2+}, \text{Cr}^{3+}$	$\text{Cr}^{2+}, \text{Mn}^{3+}$	$\text{Mn}^{2+}, \text{Fe}^{3+}$	$\text{Fe}^{2+}, \text{Co}^{3+}$	$\text{Co}^{2+}, \text{Ni}^{3+}$	$\text{Ni}^{2+}, \text{Pt}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$
HIGH SPIN	$e_g$	---	---	---	↑ --	↑↑ --	↑↑ --	↑↑ --	↑↑ --	↑↑ --	↑↑↑↓ --
	$t_{2g}$	↑ --	↑↑ --	↑↑↑ --	↑↑↑ --	↑↑↑ --	↑↑↑ --	↑↑↑ --	↑↑↑ --	↑↑↑ --	↑↑↑ --
	CFSE	$-\frac{2}{5} \Delta_o$	$-\frac{4}{5} \Delta_o$	$-\frac{6}{5} \Delta_o$	$-\frac{3}{5} \Delta_o$	0	$-\frac{2}{5} \Delta_o$	$-\frac{4}{5} \Delta_o$	$-\frac{6}{5} \Delta_o$	$-\frac{3}{5} \Delta_o$	0
LOW SPIN	$e_g$				---	---	---	↑ --			
	$t_{2g}$				↓↑ --	↓↑↓↑ --	↓↑↓↑ --	↓↑↓↑ --			
	CFSE	Same as high spin			$-\frac{8}{5} \Delta_o$	$-\frac{10}{5} \Delta_o$	$-\frac{12}{5} \Delta_o$	$-\frac{9}{5} \Delta_o$	Same as high spin		

CFSE, Crystal field stabilization energies.

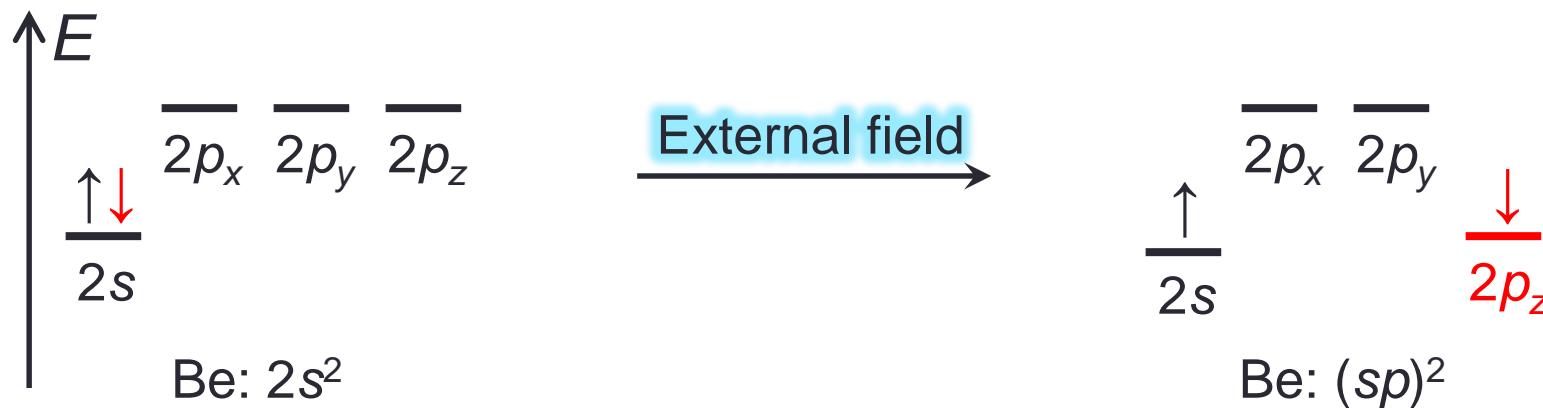
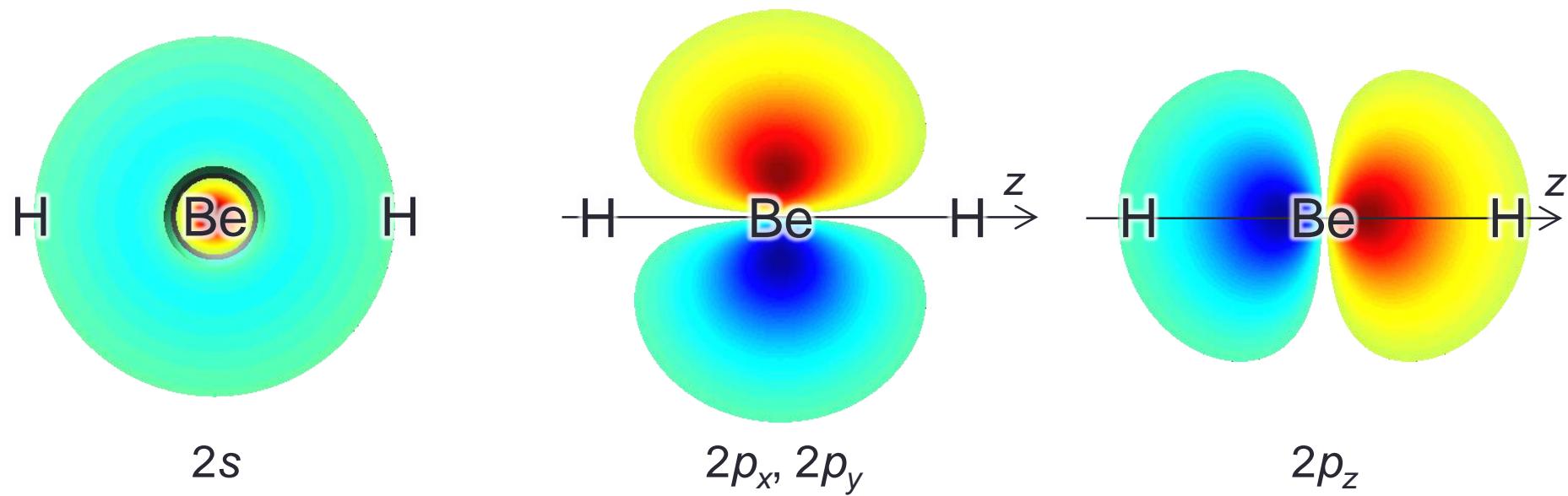
# Tetrahedral Crystal Field



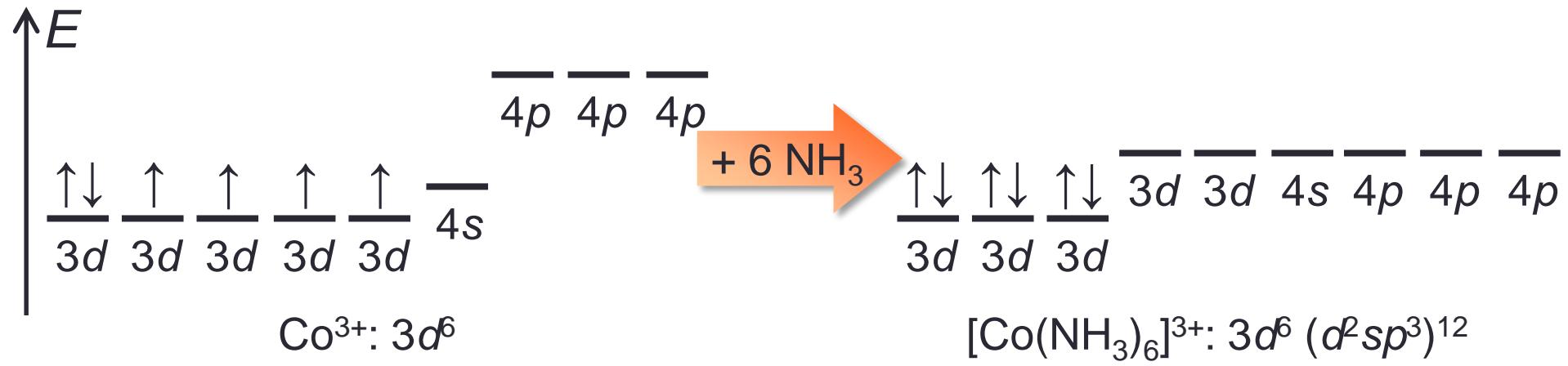
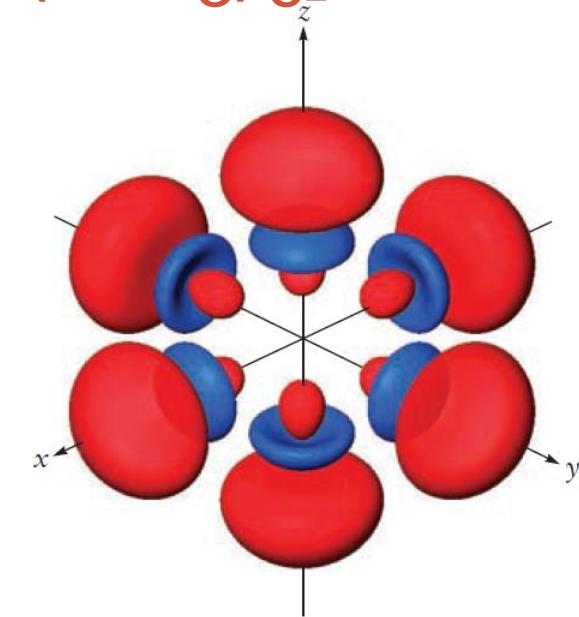
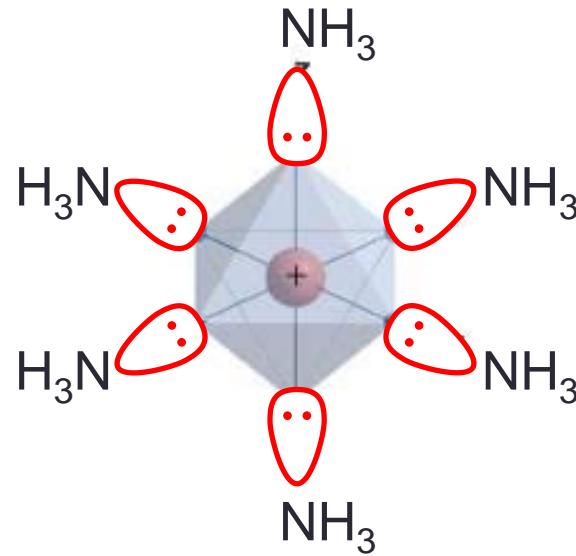
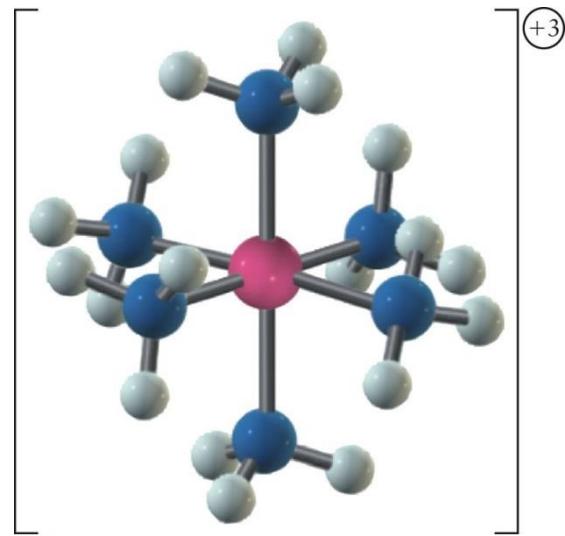
# Outline

- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
  - Nature of coordination bonding: Lewis acid-base reaction
  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - **Coordination Theory**
    - Crystal-field theory
    - **Hybridization Valence Bond theory**
    - Ligand-field theory
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

# Orbital Hybridization in BeH<sub>2</sub>



# Orbital Hybridization in $[\text{Co}(\text{NH}_3)_6]^{3+}$



# Hybridization Valence Bond theory

- Comply with VSEPR theory

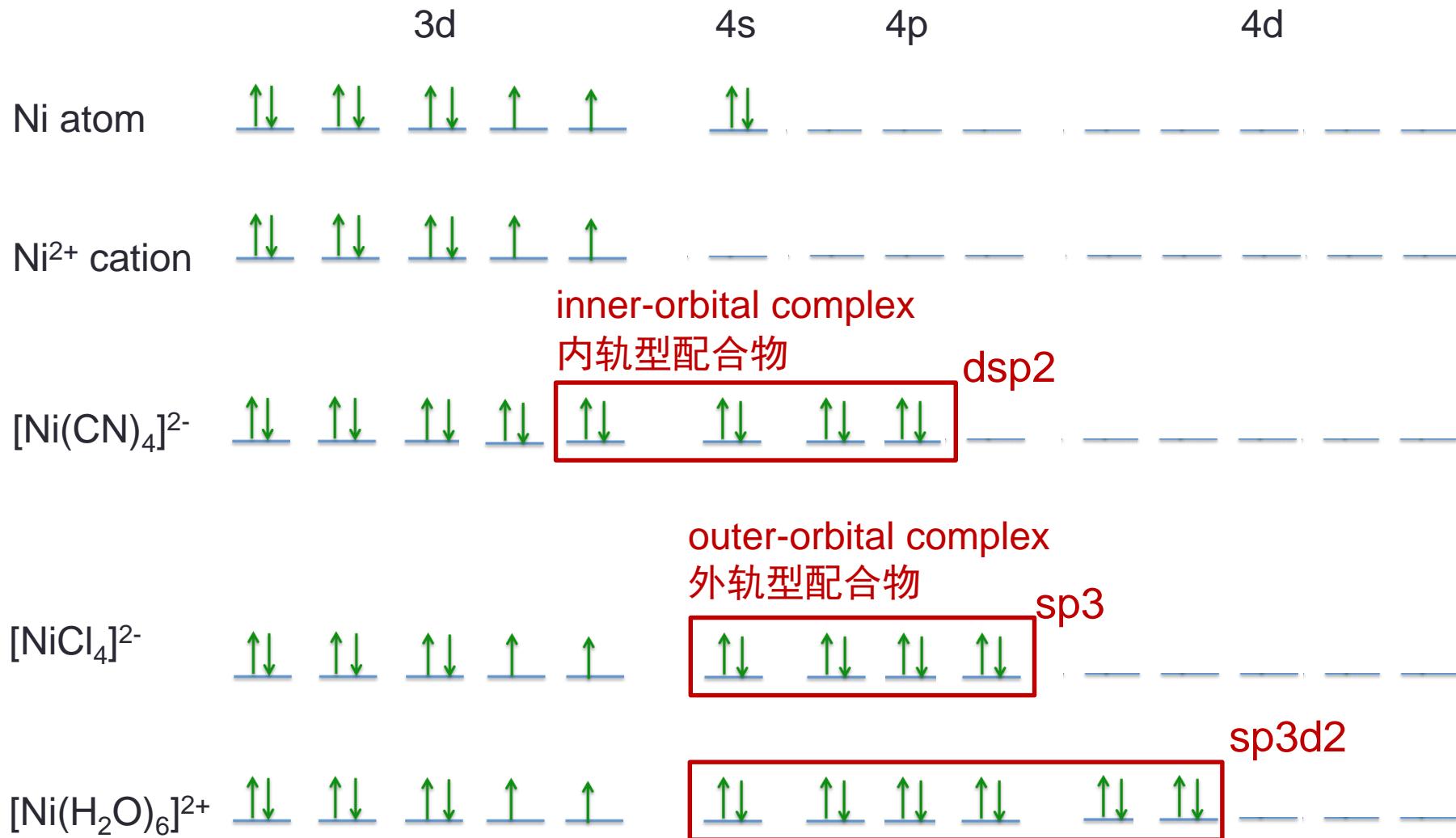
TABLE 8.7

Examples of Hybrid Orbitals and Bonding in Complexes

Coordination Number	Hybrid Orbital	Configuration	Examples
2	$sp$	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$
3	$sp^2$	Trigonal planar	$\text{BF}_3, \text{NO}_3^-, [\text{Ag}(\text{PR}_3)_3]^+$
4	$sp^3$	Tetrahedral	$\text{Ni}(\text{CO})_4, [\text{MnO}_4]^-$ , $[\text{Zn}(\text{NH}_3)_4]^{2+}$
4	$dsp^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}, [\text{Pt}(\text{NH}_3)_4]^{2+}$
5	$dsp^3$	Trigonal bipyramidal	$\text{TaF}_5, [\text{CuCl}_5]^{3-}$ , $[\text{Ni}(\text{PEt}_3)_2\text{Br}_3]$
6	$d^2sp^3$	Octahedral	$[\text{Co}(\text{NH}_3)_6]^{3+}, [\text{PtCl}_6]^{2-}$

From G.E. Kimball, Directed valence. *J. Chem. Phys.* 1940, 8, 188.

# Orbital Hybridization for TM Complex



# Inner-orbital and Outer-orbital Complex

- For  $(n-1)d^{10}$  ions, only use ns and np orbitals
  - $\text{Ni}^0; \text{Cu}^+, \text{Ag}^+, \text{Au}^+; \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}$
  - $\text{sp}$ :  $[\text{CuCl}_2]^-$ ,  $[\text{Ag}(\text{NH}_3)_2]^+$ ,  $[\text{Au}(\text{CN})_2]^-$ ...
  - $\text{sp}^2$ :  $[\text{Cu}(\text{SPMe}_3)_3]^+$ ,  $[\text{Ag}(\text{PR})_3]^+$ ...
  - $\text{sp}^3$ :  $\text{Ni}(\text{CO})_4$ ,  $[\text{Cu}(\text{CN})_4]^{3-}$ ,  $[\text{Zn}(\text{CN})_4]^{2-}$ ,  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ ...
- For  $d^8$ ,  $\text{dsp}^2$  hybridization is general
  - $\text{Pd}^{2+}, \text{Pt}^{2+}, \text{Au}^{3+}$
  - $[\text{PdCl}_4]^{2-}, [\text{PtCl}_4]^{2-}, [\text{AuCl}_4]^-$
  - $[\text{Pd}(\text{NH}_3)_4]^{2+}, [\text{Pt}(\text{NH}_3)_4]^{2+}$
  - $[\text{Pd}(\text{CN})_4]^{2-}, [\text{Pt}(\text{CN})_4]^{2-}, [\text{Au}(\text{CN})_4]^-$



3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

# Inner-orbital and Outer-orbital Complex

- For  $d^4$  -  $d^7$ ,  $d^2sp^3$  and  $sp^3d^2$  hybridization is general
- Depends on the electronegativity of the ligands, generally
  - $F^-$  and  $H_2O$  ligands lead to  $sp^3d^2$
  - $CN^-$  ligands lead to  $d^2sp^3$
  - $NH_3$  is in between, for  $M^{2+}$  forms  $sp^3d^2$ , for  $M^{3+}$  forms  $d^2sp^3$ .

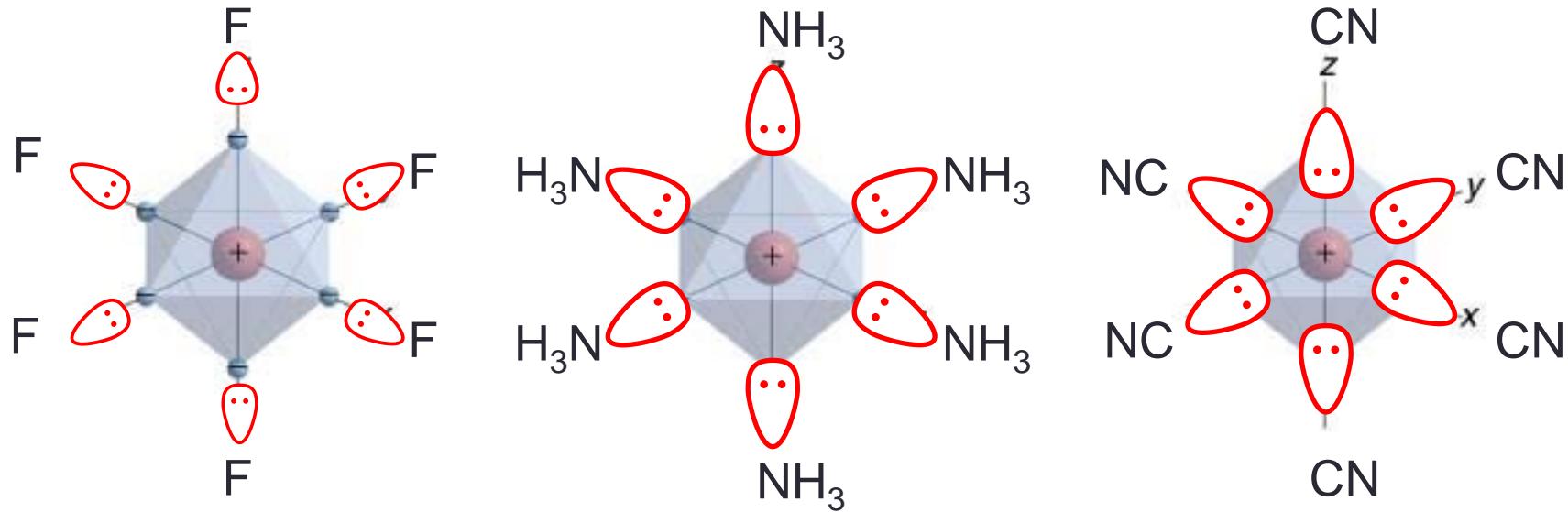


表 19-5 若干第一过渡系金属 6 配位配合物的键型、电子结构和磁学性质

离子的 电子构型	离子	配离子	杂化轨道 道类型	配离子的电子结构				不成对 电子数	理论	磁矩( $\mu_B$ )
				3d	4s	4p	4d			
3d <sup>4</sup>	Cr <sup>2+</sup>	[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>					4	4.90	4.8~5.0
		[Cr(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>2</sup> sp <sup>3</sup>					2	2.83	3.22
3d <sup>5</sup>	Mn <sup>3+</sup>	[MnF <sub>6</sub> ] <sup>3-</sup>	sp <sup>3</sup> d <sup>2</sup>					4	4.90	—
		[Mn(CN) <sub>6</sub> ] <sup>3-</sup>	d <sup>2</sup> sp <sup>3</sup>					2	2.83	3.0
3d <sup>6</sup>	Mn <sup>2+</sup>	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>					5	5.92	5.9
		[Mn(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>2</sup> sp <sup>3</sup>					1	1.73	2.0
3d <sup>7</sup>	Fe <sup>3+</sup>	[FeF <sub>6</sub> ] <sup>3-</sup>	sp <sup>3</sup> d <sup>2</sup>					5	5.92	5.9
		[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	sp <sup>3</sup> d <sup>2</sup>					5	5.92	5.9
3d <sup>8</sup>		[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	d <sup>2</sup> sp <sup>3</sup>					1	1.73	2.33
	Fe <sup>2+</sup>	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>					4	4.90	5.25
3d <sup>9</sup>		[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>2</sup> sp <sup>3</sup>					0	0.00	0.00
	Co <sup>3+</sup>	[CoF <sub>6</sub> ] <sup>3-</sup>	sp <sup>3</sup> d <sup>2</sup>					4	4.90	5.3
3d <sup>10</sup>		[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	d <sup>2</sup> sp <sup>3</sup>					0	0.00	0.00
		[Co(CN) <sub>6</sub> ] <sup>3-</sup>	d <sup>2</sup> sp <sup>3</sup>					0	0.00	0.00
3d <sup>11</sup>	Co <sup>2+</sup>	[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>					3	3.88	5.06
		[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>					3	3.88	4.96

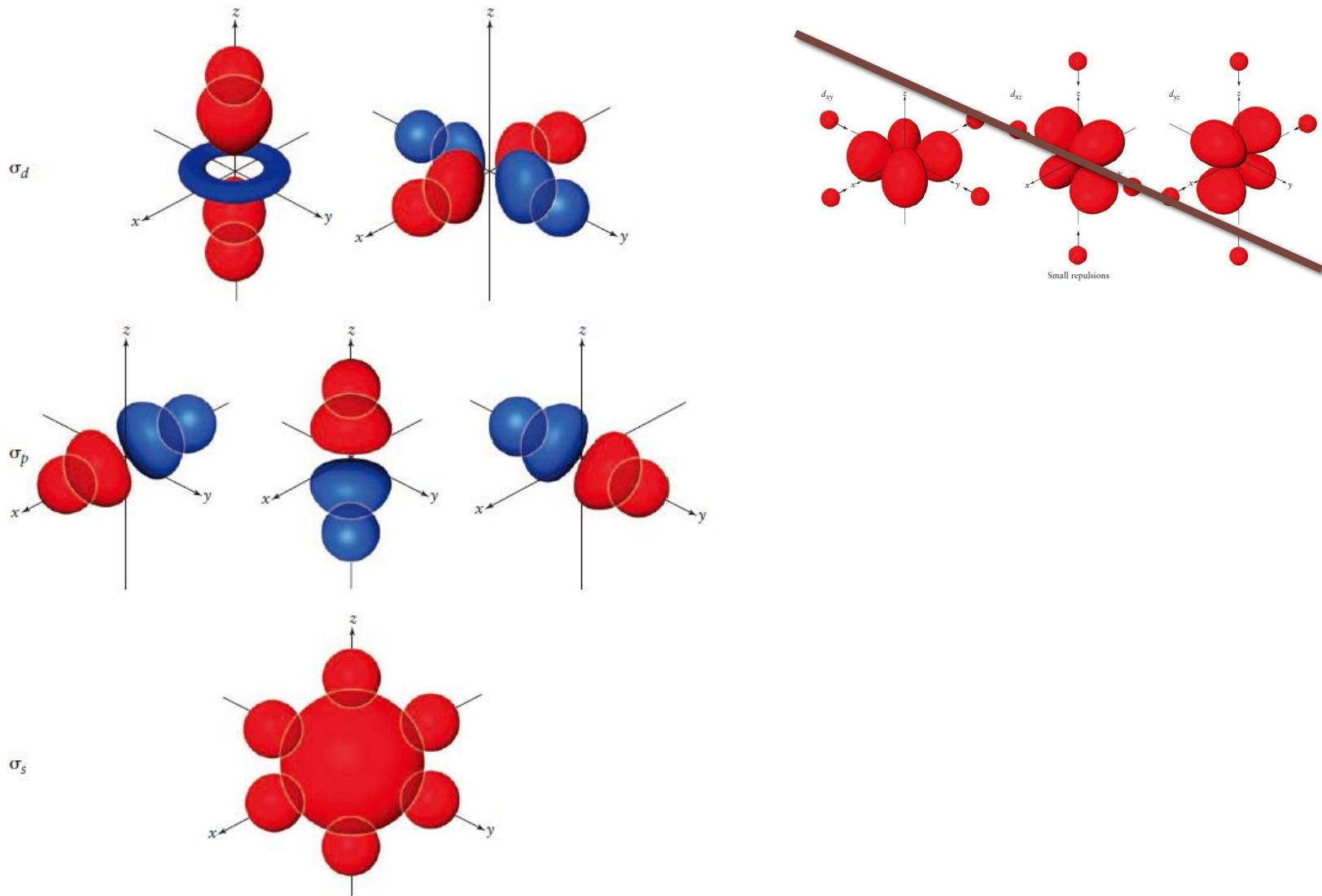
高自旋, high spin

低自旋, low spin

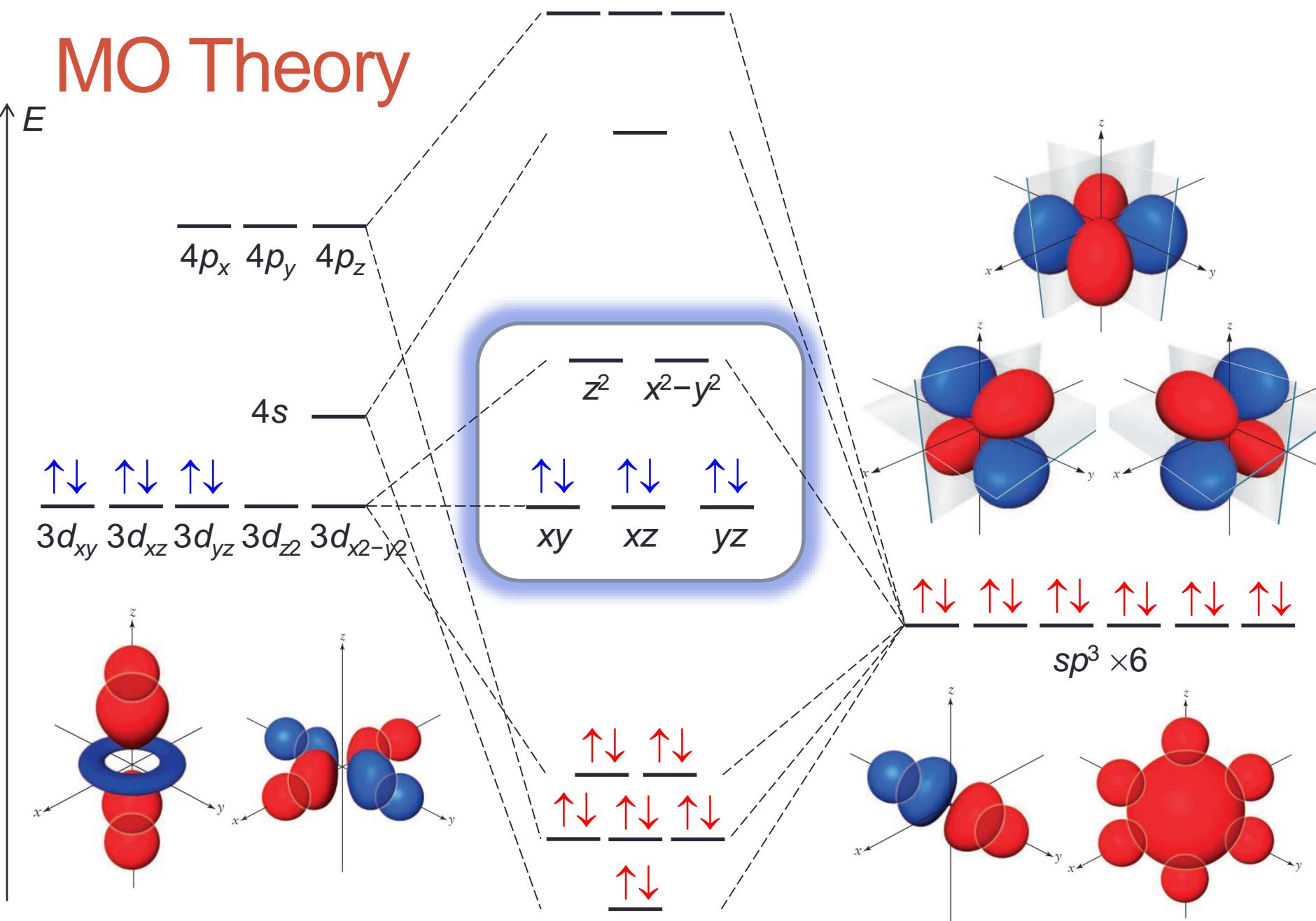
# Outline

- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
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  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - Coordination Theory
    - Crystal-field theory
    - Hybridization Valence Bond theory
    - **Ligand-field theory**
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

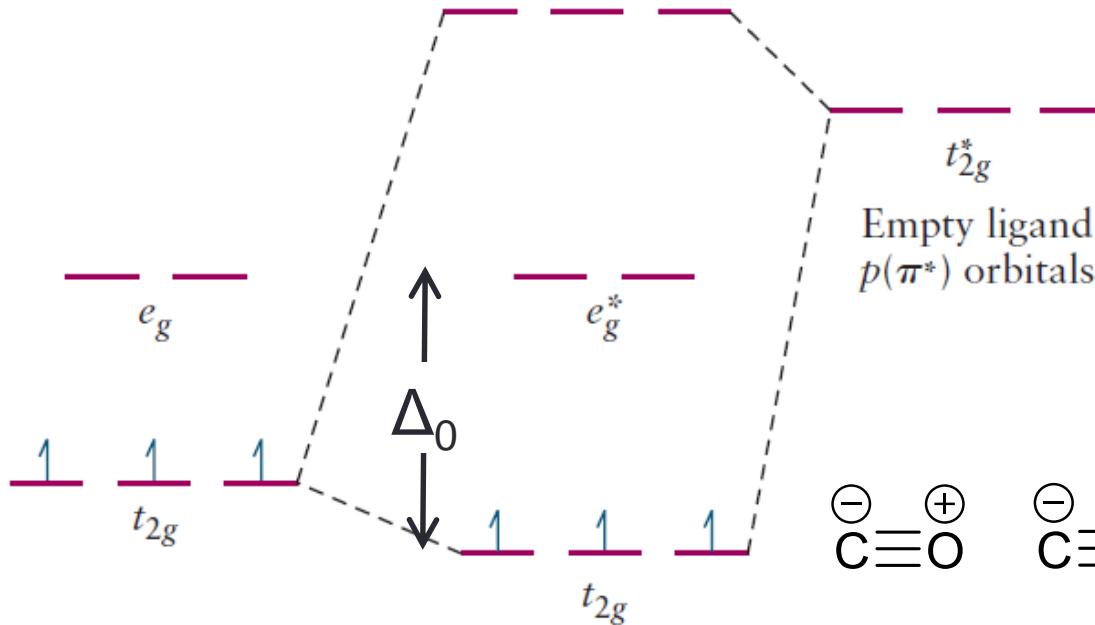
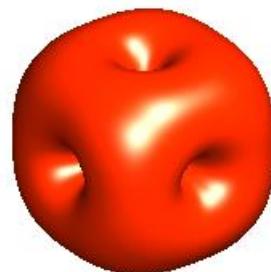
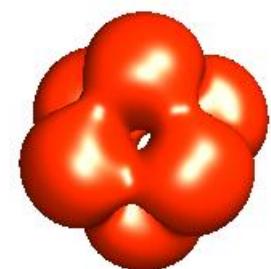
# Ligand-field theory based on MO



# MO Theory



# Strongest Ligands: $\pi$ Acceptors



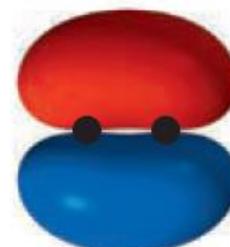
Empty ligand  
 $p(\pi^*)$  orbitals



CO and CN<sup>-</sup> are strongest ligands

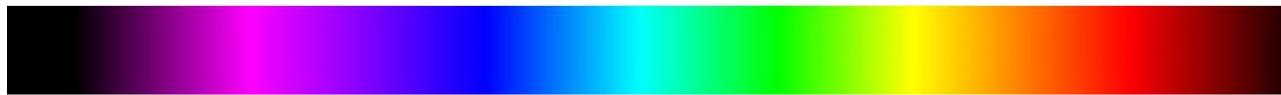


Filled ligand  
 $p(\pi)$  orbitals

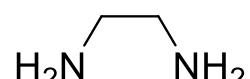
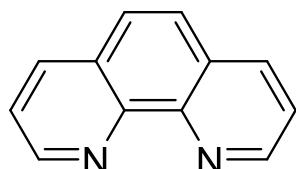


# The Spectrochemical Series 光谱化学序列

Absorption

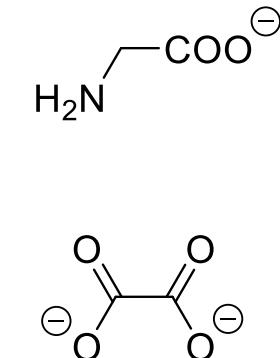


Appearance

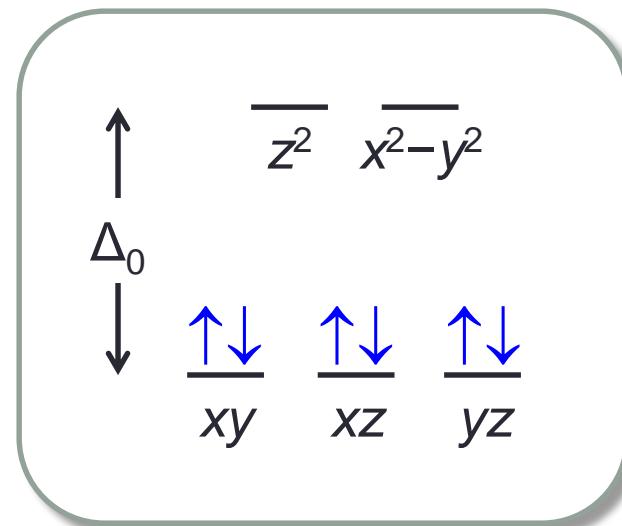
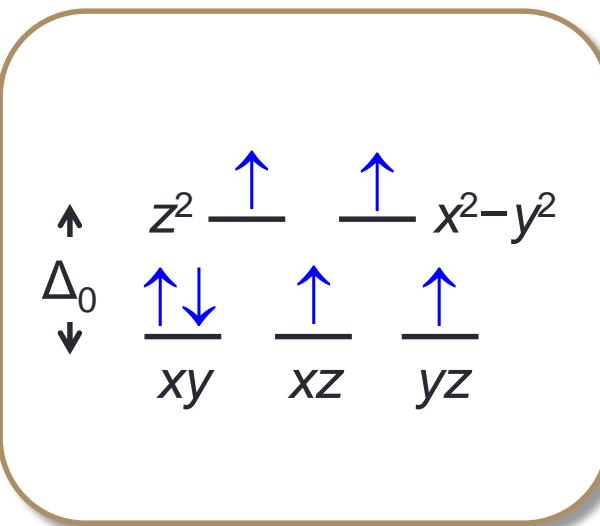


- a.  $[\text{Co}(\text{CN})_6]^{3-}$
- b.  $[\text{Co}(\text{NO}_2)_6]^{3-}$
- c.  $[\text{Co}(\text{phen})_3]^{3+}$
- d.  $[\text{Co}(\text{en})_3]^{3+}$
- e.  $[\text{Co}(\text{NH}_3)_6]^{3+}$

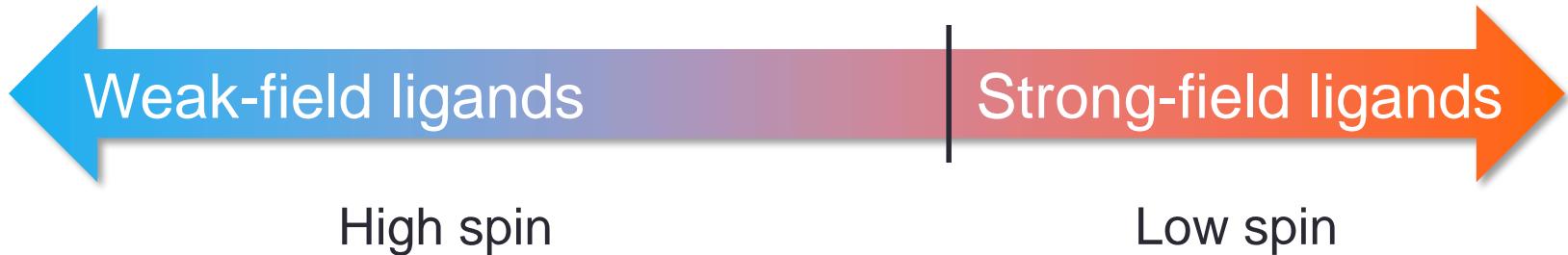
- f.  $[\text{Co}(\text{gly})_3]$
- g.  $[\text{Co}(\text{H}_2\text{O})_3]^{3+}$
- h.  $[\text{CoF}_6]^{3-}$
- i.  $[\text{Co}(\text{ox})_3]^{3-}$



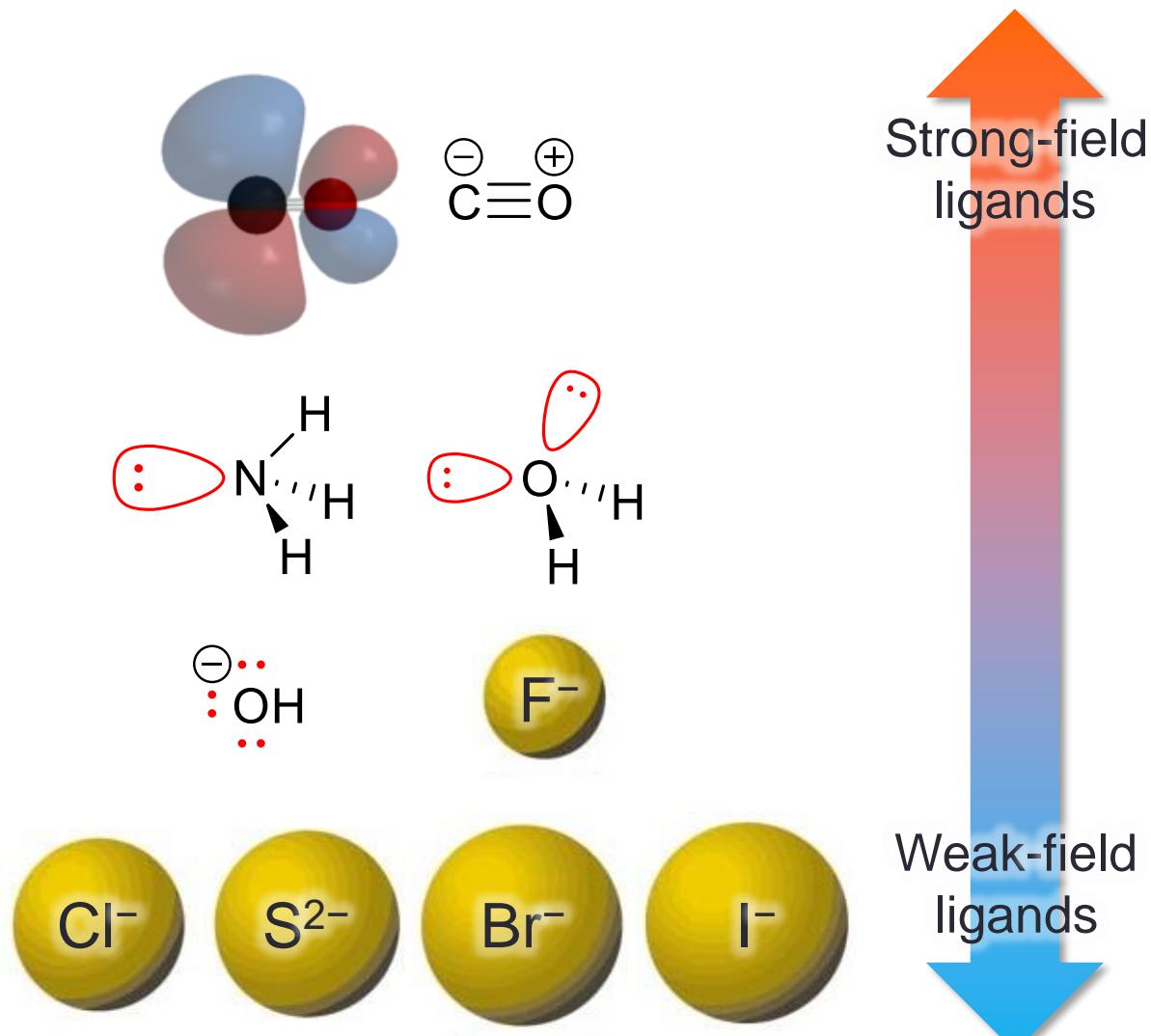
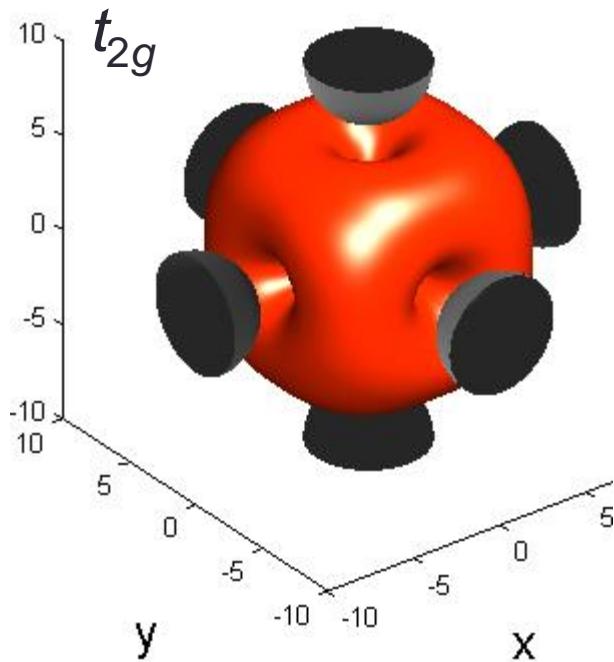
# The Spectrochemical Series (2)



$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < \text{NH}_3 < \text{CN}^- \approx \text{CO}$



# The Spectrochemical Series (3)



# Outline

- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
  - Nature of coordination bonding: Lewis acid-base reaction
  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - Coordination Theory
    - Crystal-field theory
    - Hybridization Valence Bond theory
    - Ligand-field theory
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

# Heat of Hydration

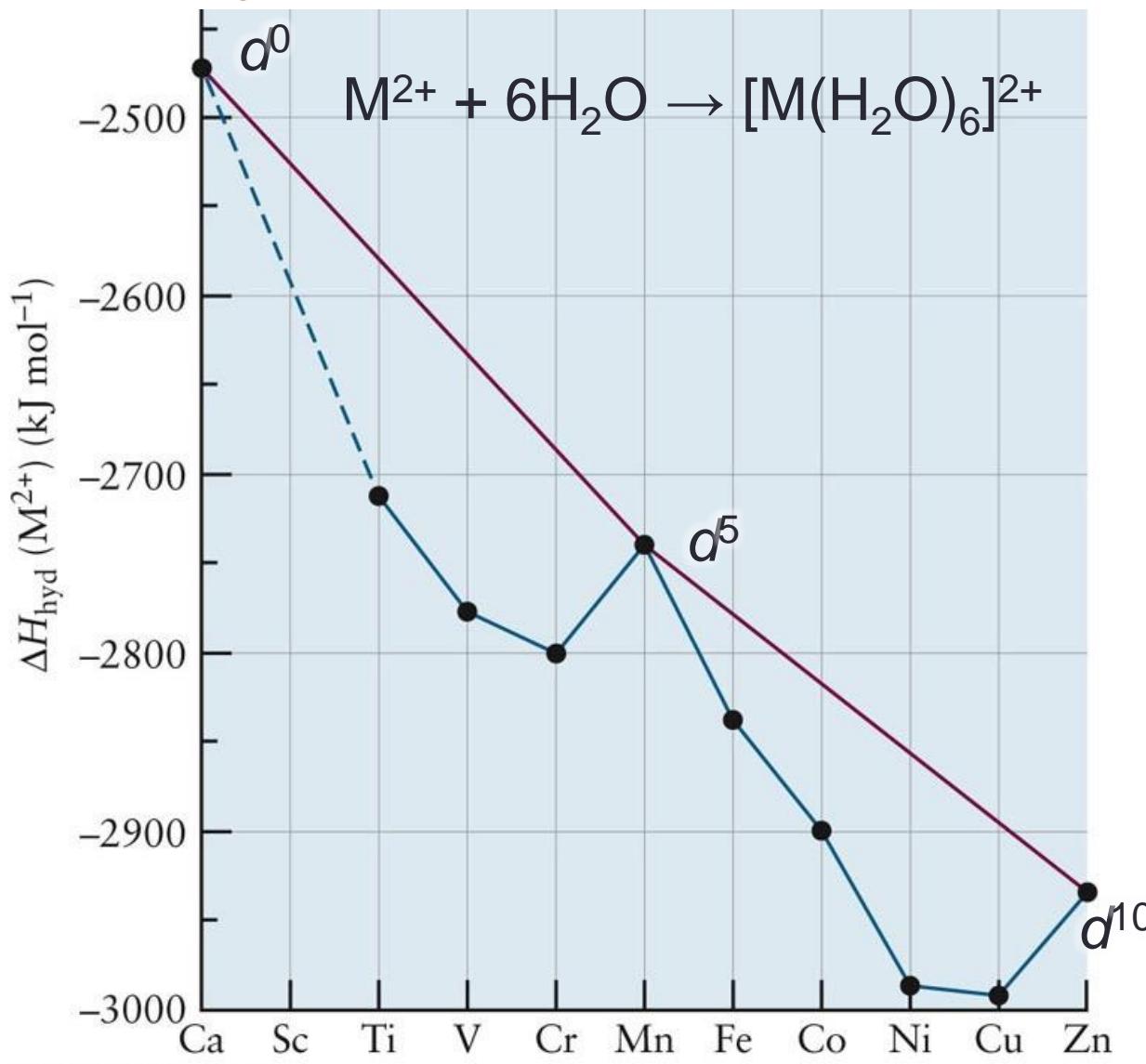
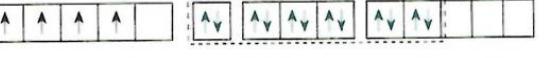
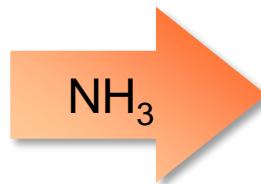
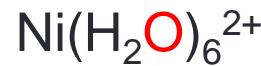


表 19-5 若干第一过渡系金属 6 配位配合物的键型、电子结构和磁学性质

离子的 电子构型	离子	配离子	杂化轨道 道类型	配离子的电子结构				不成对 电子数	理论 磁矩( $\mu_B$ )	观察 磁矩( $\mu_B$ )
				3d	4s	4p	4d			
3d <sup>4</sup>	Cr <sup>2+</sup>	[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>		4	4.90	4.8~5.0			
		[Cr(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>2</sup> sp <sup>3</sup>		2	2.83	3.22			
3d <sup>5</sup>	Mn <sup>3+</sup>	[MnF <sub>6</sub> ] <sup>3-</sup>	sp <sup>3</sup> d <sup>2</sup>		4	4.90	—			
		[Mn(CN) <sub>6</sub> ] <sup>3-</sup>	d <sup>2</sup> sp <sup>3</sup>		2	2.83	3.0			
3d <sup>6</sup>	Mn <sup>2+</sup>	[Mn(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>		5	5.92	5.9			
		[Mn(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>2</sup> sp <sup>3</sup>		1	1.73	2.0			
3d <sup>7</sup>	Fe <sup>3+</sup>	[FeF <sub>6</sub> ] <sup>3-</sup>	sp <sup>3</sup> d <sup>2</sup>		5	5.92	5.9			
		[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	sp <sup>3</sup> d <sup>2</sup>		5	5.92	5.9			
3d <sup>8</sup>	Fe <sup>2+</sup>	[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>		4	4.90	5.25			
		[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	d <sup>2</sup> sp <sup>3</sup>		0	0.00	0.00			
3d <sup>9</sup>	Co <sup>3+</sup>	[CoF <sub>6</sub> ] <sup>3-</sup>	sp <sup>3</sup> d <sup>2</sup>		4	4.90	5.3			
		[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	d <sup>2</sup> sp <sup>3</sup>		0	0.00	0.00			
3d <sup>10</sup>	Co <sup>2+</sup>	[Co(CN) <sub>6</sub> ] <sup>3-</sup>	d <sup>2</sup> sp <sup>3</sup>		0	0.00	0.00			
		[Co(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>		3	3.88	5.06			
		[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	sp <sup>3</sup> d <sup>2</sup>		3	3.88	4.96			

# Stability and Reactivity



Ligand substitution reactions proceed sequentially, and they can usually be stopped at intermediate stages by controlling the reaction conditions



# Outline

- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
  - Nature of coordination bonding: Lewis acid-base reaction
  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
  - Coordination Theory
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    - Ligand-field theory
  - Coordination Complexes Properties
    - Hydration of TM Cations
    - Stability and Reactivity
    - Color and spectroscopy
    - Magnetism
- f-block Metal

# Color and spectroscopy

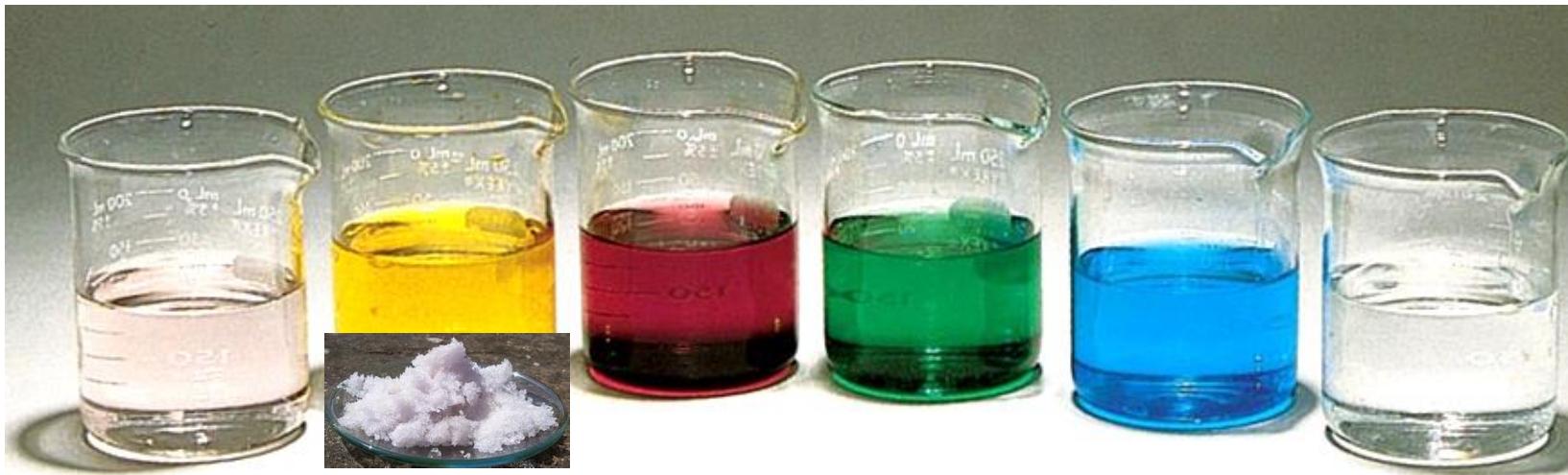


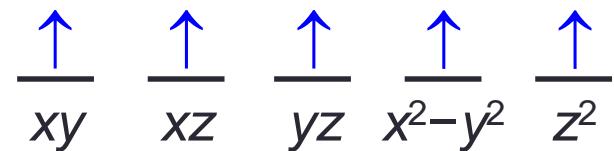
TABLE 8.5

Electron Configurations and Crystal Field Stabilization Energies for High- and Low-Spin Octahedral Complexes

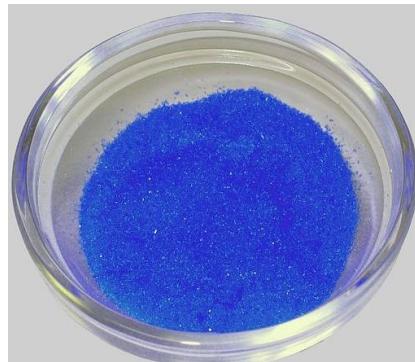
Configuration		$d^1$	$d^2$	$d^3$	$d^4$	$d^5$	$d^6$	$d^7$	$d^8$	$d^9$	$d^{10}$
Examples		$\text{Ti}^{3+}$	$\text{Ti}^{2+}, \text{V}^{3+}$	$\text{V}^{2+}, \text{Cr}^{3+}$	$\text{Cr}^{2+}, \text{Mn}^{3+}$	$\text{Mn}^{2+}, \text{Fe}^{3+}$	$\text{Fe}^{2+}, \text{Co}^{3+}$	$\text{Co}^{2+}, \text{Ni}^{3+}$	$\text{Ni}^{2+}, \text{Pt}^{2+}$	$\text{Cu}^{2+}$	$\text{Zn}^{2+}$
HIGH SPIN	$e_g$	---	---	---	↑ —	↑↑ —	↑↑ —	↑↑ —	↑↑ —	↑↑ —	
	$t_{2g}$	↑ —	↑↑ —	↑↑↑ —	↑↑↑ —	↑↑↑ —	↑↑↑ —	↑↑↑ —	↑↑↑ —	↑↑↑ —	
	CFSE	$-\frac{2}{5} \Delta_o$	$-\frac{4}{5} \Delta_o$	$-\frac{6}{5} \Delta_o$	$-\frac{3}{5} \Delta_o$	0	$-\frac{2}{5} \Delta_o$	$-\frac{4}{5} \Delta_o$	$-\frac{6}{5} \Delta_o$	$-\frac{3}{5} \Delta_o$	0

# Manganese: An Outlier

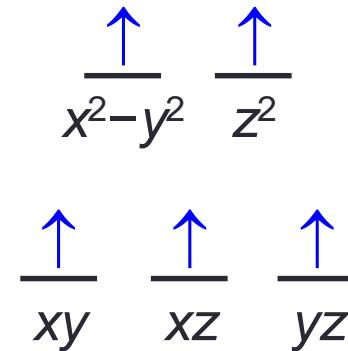
$\text{Mn}^{2+}$ :  $3d^5$  is **half-filled** and inert.  
 $\text{Mn}^{2+}$  is similar to  $\text{Ca}^{2+}$  and  $\text{Zn}^{2+}$ .



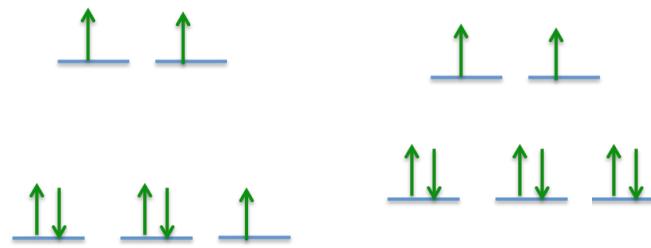
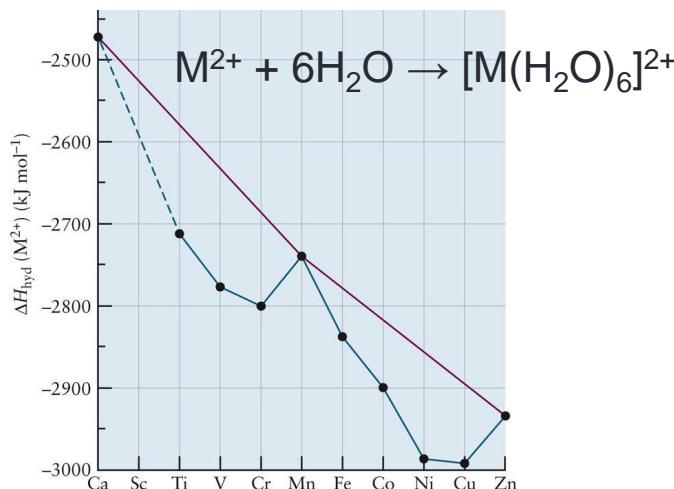
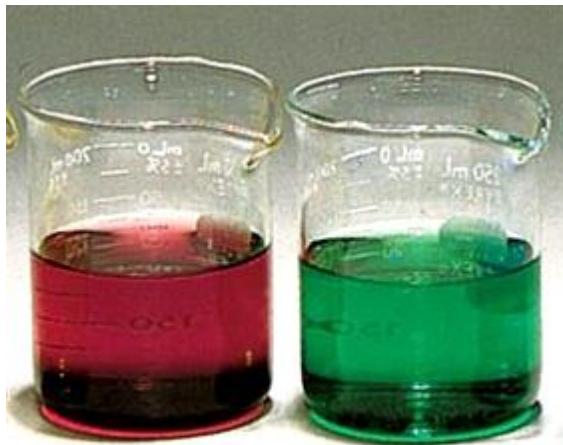
$\text{MnSO}_4 \cdot \text{H}_2\text{O}$



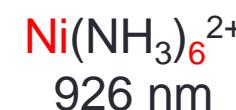
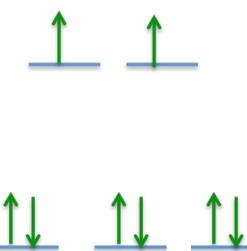
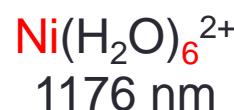
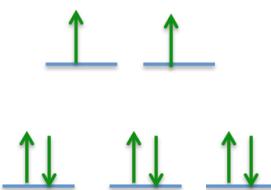
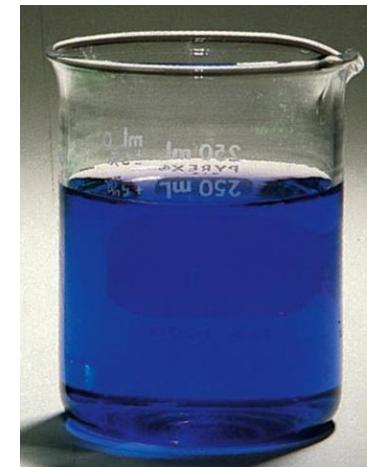
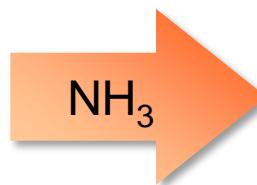
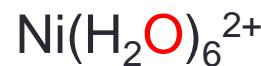
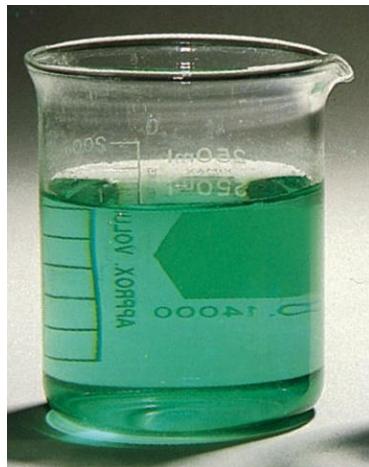
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$



# Color and spectroscopy



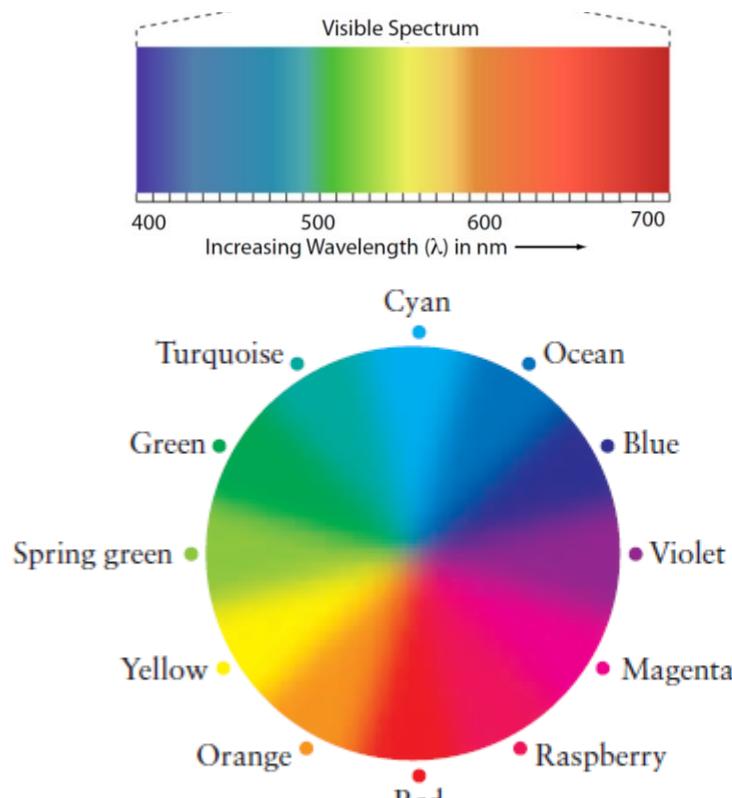
# Color and spectroscopy



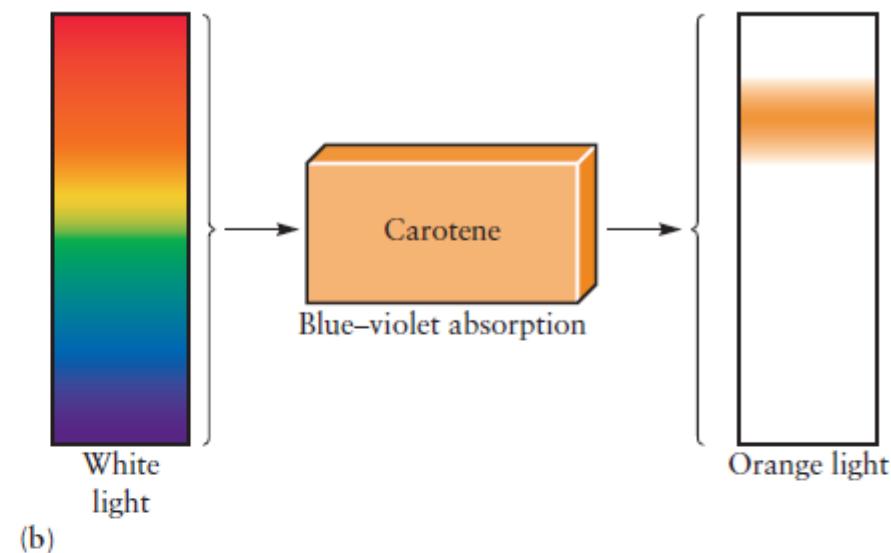
# Color and spectroscopy



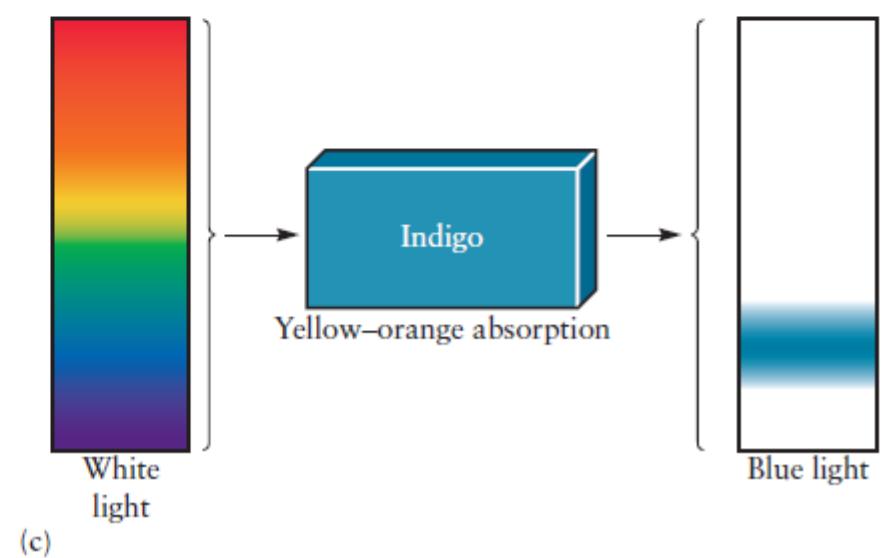
# Complementary Colors 互补色



(a)



(b)

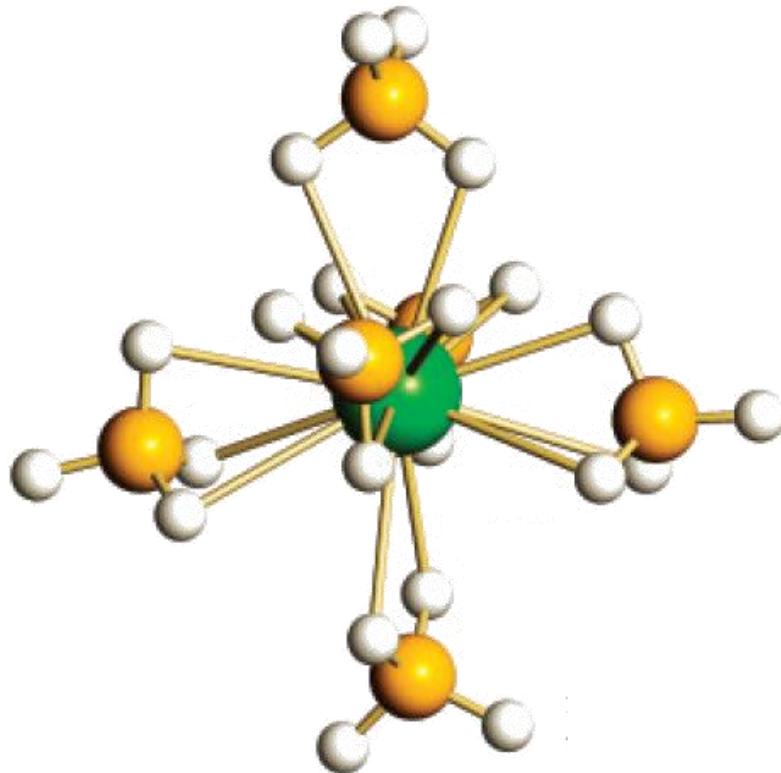


(c)

# Outline

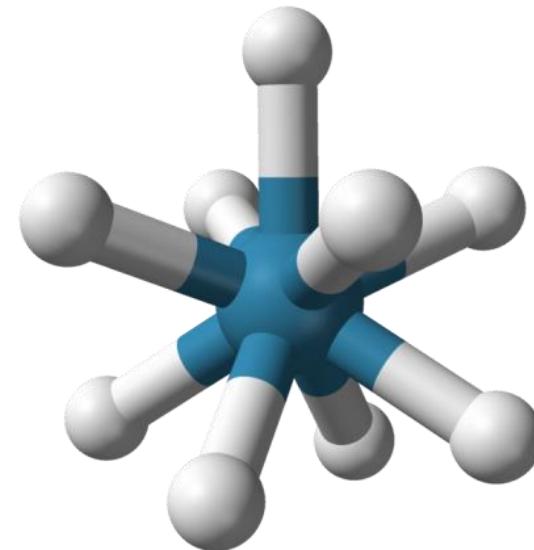
- Metal
  - Metallic bond and physical properties
- p-block Metal
  - Al, Ga, In, Tl; Ge, Sn, Pb; Sb, Bi
  - Oxide, Hydroxide, Chloride, Fluoride, Organometallic compound
- d-block Metal (Transition metal, TM)
  - General Trends, 18-electron Rule and Coordination Complexes
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  - Coordination Complexes of Fe, Co, CN<sup>-</sup>, CO, NH<sub>3</sub>, Cl<sup>-</sup>, O<sup>2-</sup>
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    - Crystal-field theory
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    - Magnetism
- f-block Metal

# f-Block Elements



钍

Thorium, after Thor



# Rare Earths 稀土 (RE)

## Rare earth = Sc + Y + Lanthanides

# Electronic Configurations (1)

镧

57	2
<b>La</b>	8
Lanthanum	18
138.90547	9
	2

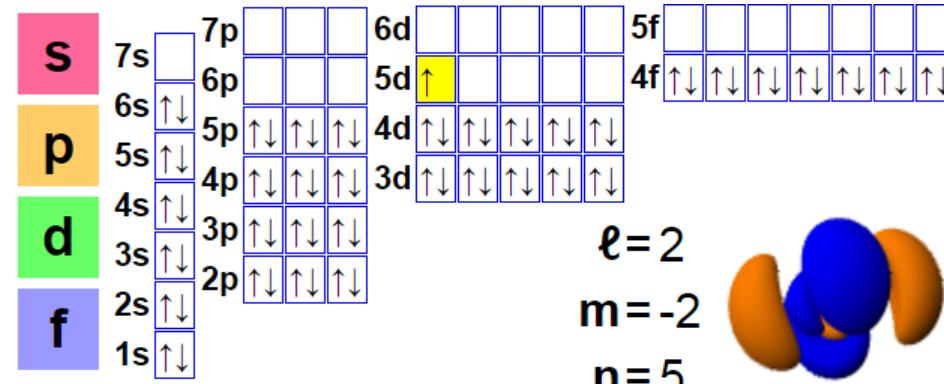
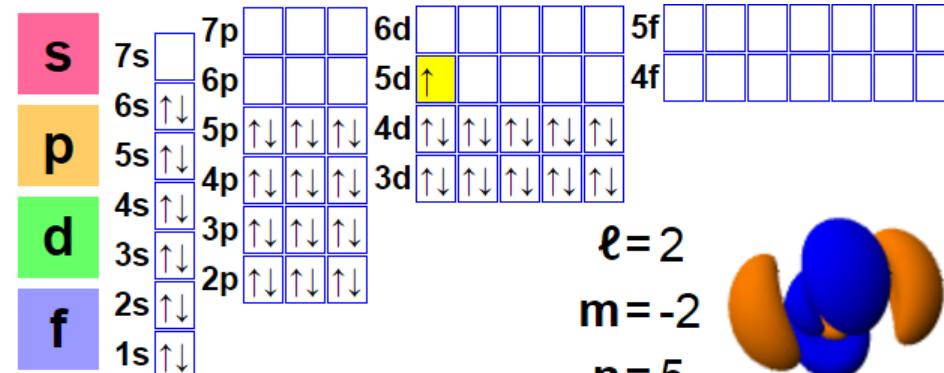
2 3

|  
| 13 elements  
|  
|

镥

71	2
<b>Lu</b>	8
Lutetium	18
174.9668	32
	9
	2

3



铈

58	2
<b>Ce</b>	8
Cerium	18
140.116	19
	9
	2

2 3 4

镨

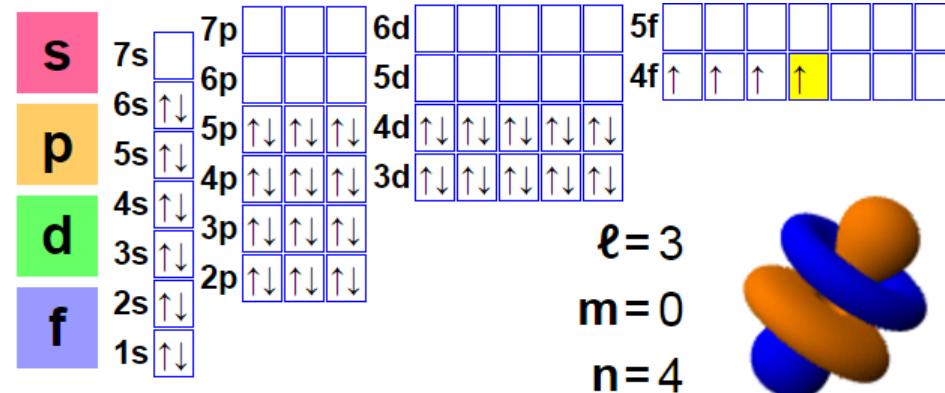
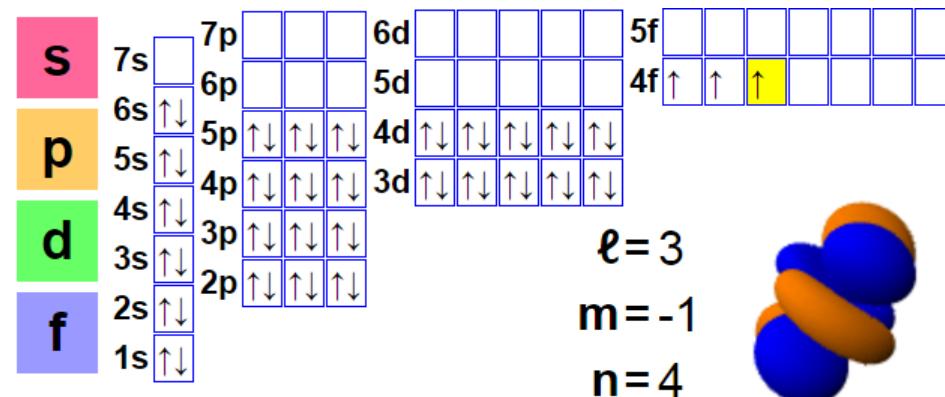
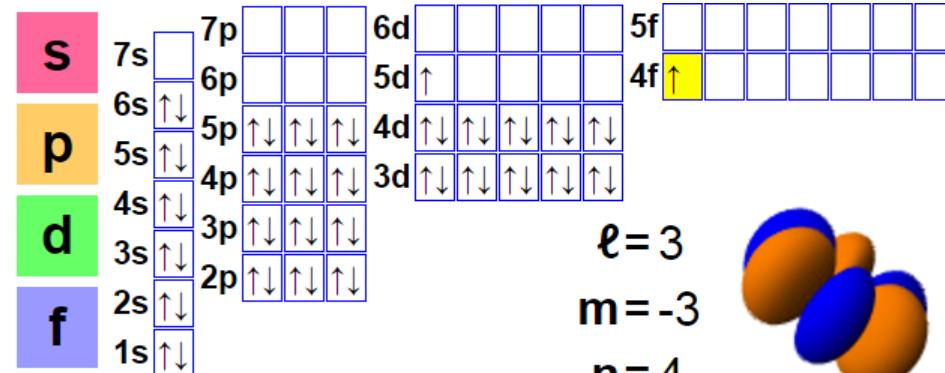
59	2
<b>Pr</b>	8
Praseodymium	18
140.90765	21
	8
	2

2 3 4

钕

60	2
<b>Nd</b>	8
Neodymium	18
144.242	22
	8
	2

2 3



钷

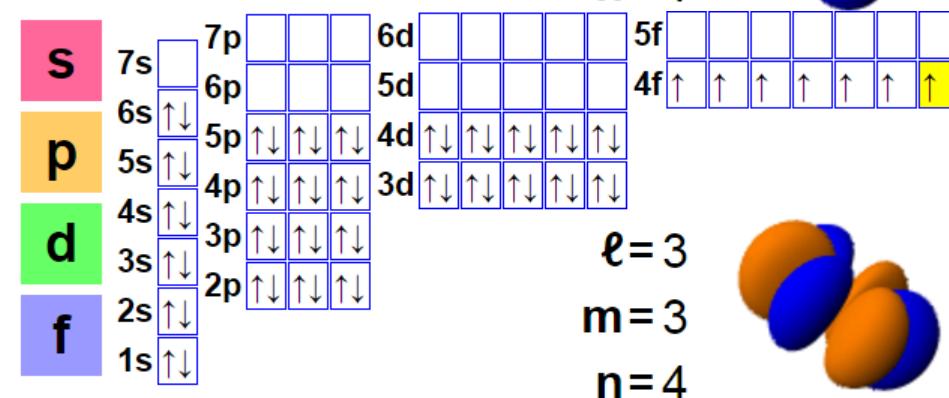
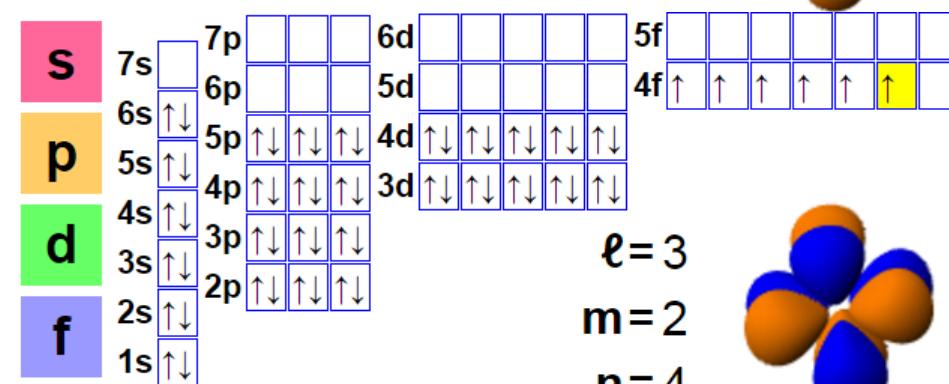
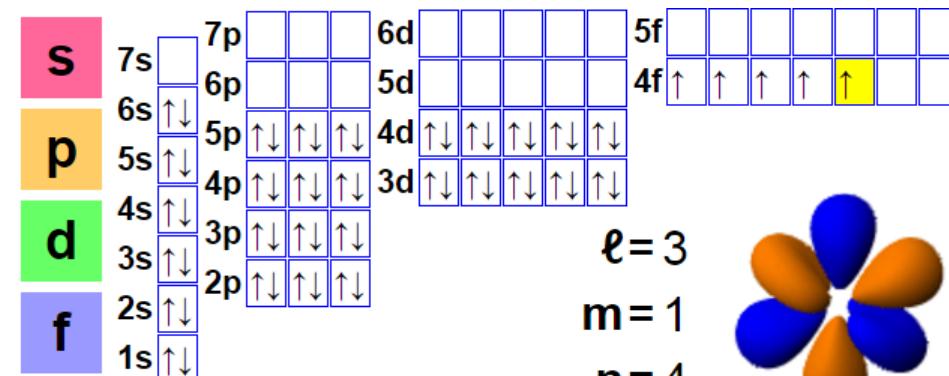
61	2 8
<b>Pm</b>	18 23
Promethium	8 2
(145)	
	3

钐

62	2 8
<b>Sm</b>	18 24
Samarium	8 2
150.36	
	2 3

铕

63	2 8
<b>Eu</b>	18 25
Europium	8 2
151.964	
	2 3



钆

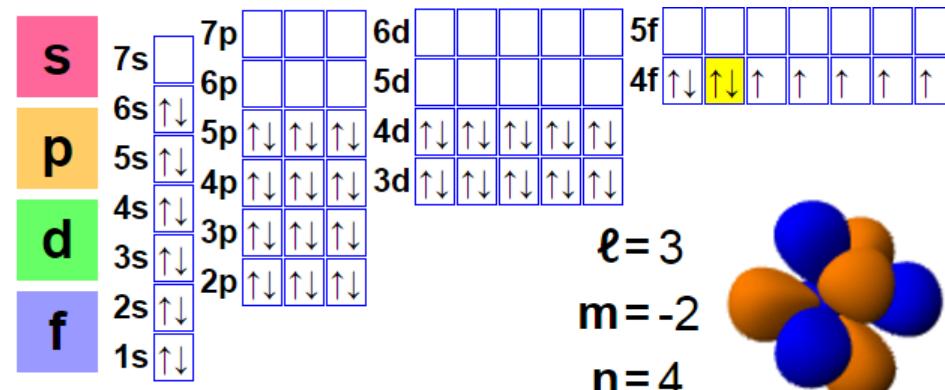
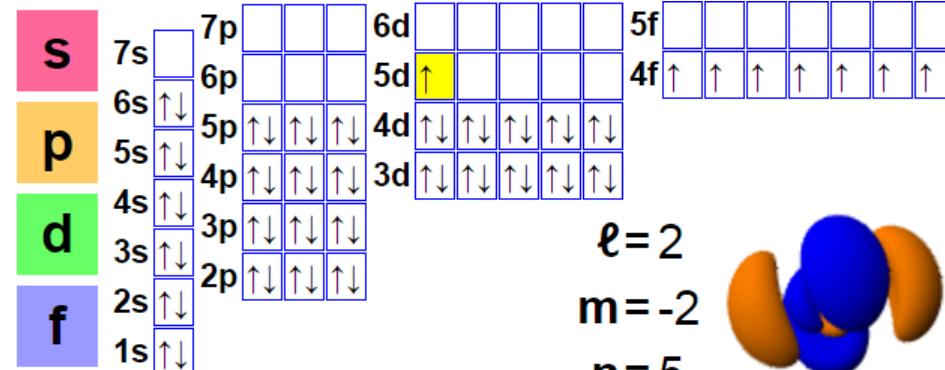
64	2
<b>Gd</b>	18
Gadolinium	9
157.25	2
	1 2 3

铽

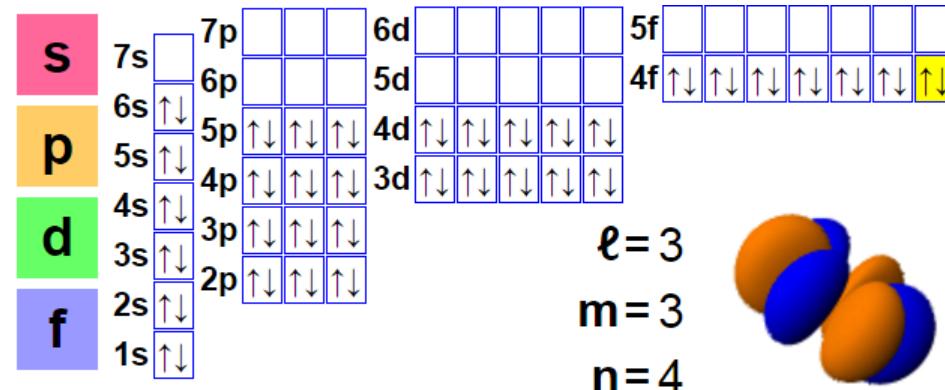
65	2
<b>Tb</b>	18
Terbium	8
158.92535	2
	1 3 4

镱

70	2
<b>Yb</b>	18
Ytterbium	8
173.054	2
	2 3



| 4 elements



# Oxidation States

Rare earth	La	Ce	Pr	Nd	Pm	Sm	Eu
$6s+5d+4f$ electrons	3	4	5	6	7	8	9
Oxidation states	+3 +4	+3 +4	+3 +4	+3	+3	+2 +3	+2 +3
$4f$ electrons in $\text{RE}^{n+}$	0	1 0	2 1	3	4	6 5	7 6

Gd	Td	Dy	Ho	Er	Tm	Yb	Lu
10	11	12	13	14	15	16	17
+3 +4	+3 +4	+3	+3	+3	+3	+2 +3	+3
7	8 7	9	10	11	12	14 13	14

# Chemical Properties

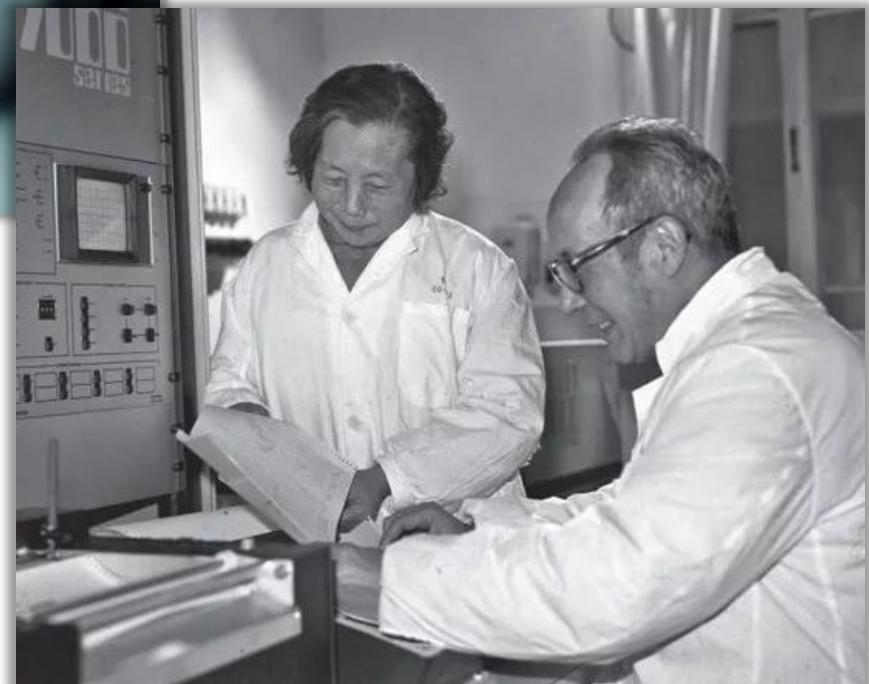
Rare earth	La	Ce	Pr	Nd	Pm	Sm	Eu
Oxidation states	+3 +4	+3 +4	+3 +4	+3	+3	+2 +3	+2 +3
r( $\text{RE}^{3+}$ ) / pm	117.2	115	113	112.3	111	109.8	108.7
Category	Light rare earths				Radio-active	Middle REs	

Gd	Td	Dy	Ho	Er	Tm	Yb	Lu
+3	+3 +4	+3	+3	+3	+3	+2 +3	+3
107.8	106.3	105.2	104.1	103	102	100.8	100.1
Middle rare earths				Heavy rare earths			



“中国稀土之父”  
徐光宪  
(1920–2015)  
串级萃取理论

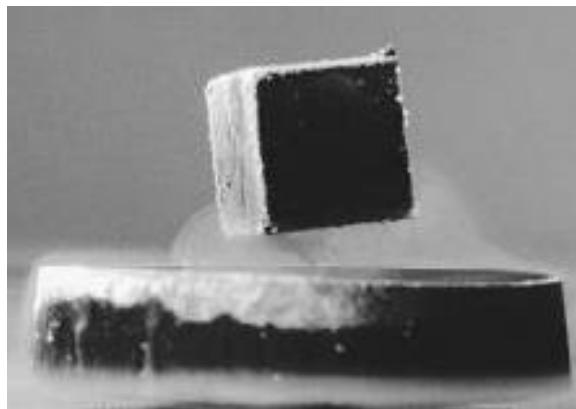
1985年，徐光宪与夫人高小霞



# Applications: Chemical

Forms very stable **oxides** and fluorides

- High m.p. and hardness
- Doping in functional ceramics and crystals



$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

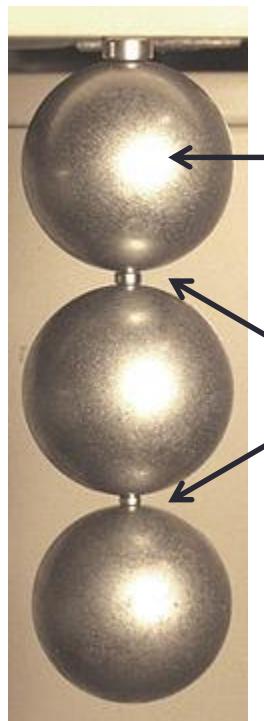


$\text{CeO}_2$   
M.p. ~2400 °C

# Applications: Functional Materials

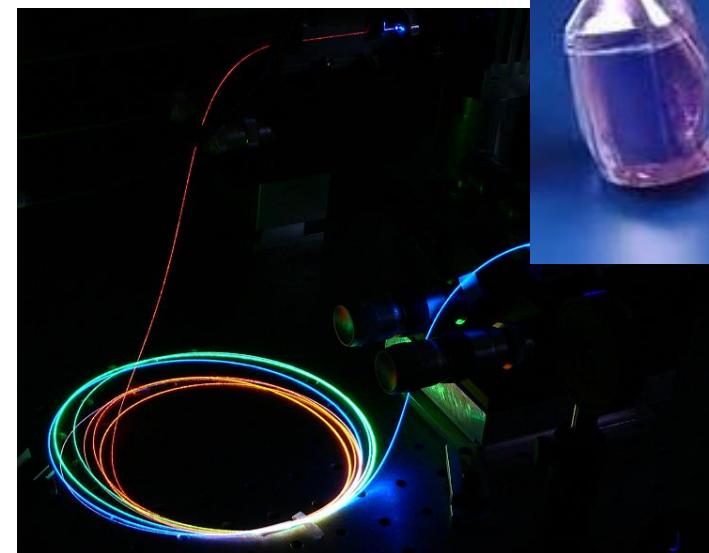
The unpaired *f* electrons are **unaffected** by chemistry

- Unlike crystal-field splitting for *d* electrons
- Optical and **magnetic** properties under extreme conditions



Steel balls

NdFeB magnets

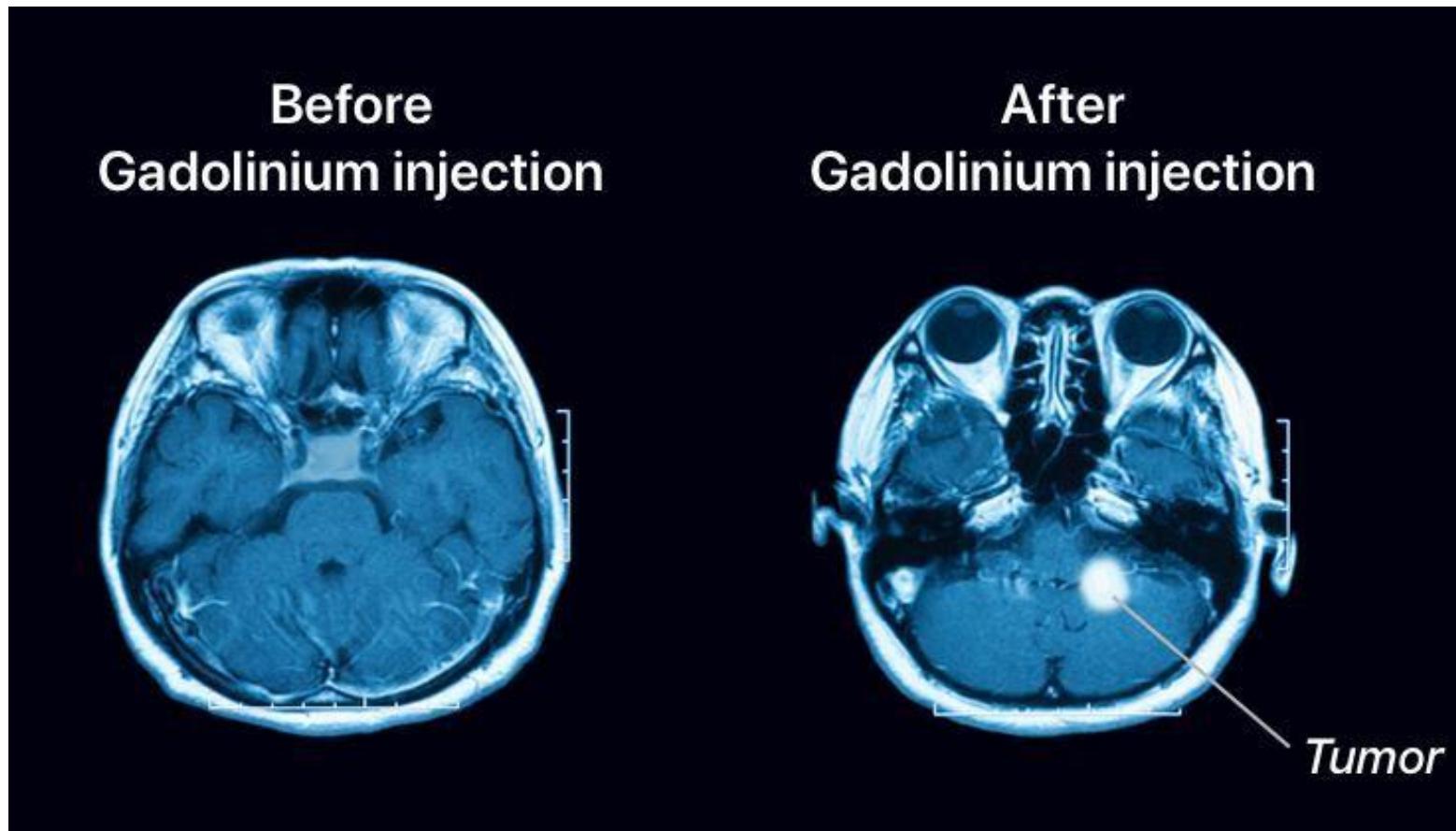


Er-doped optical fibers

Nd:YAG laser crystals



# Applications: Functional Materials



NMR imaging (**Gd**)

Next lecture Series: Spectroscopy & Photochemistry  
Reading: OGB8 §20

