Transition Metals and Coordination Chemistry

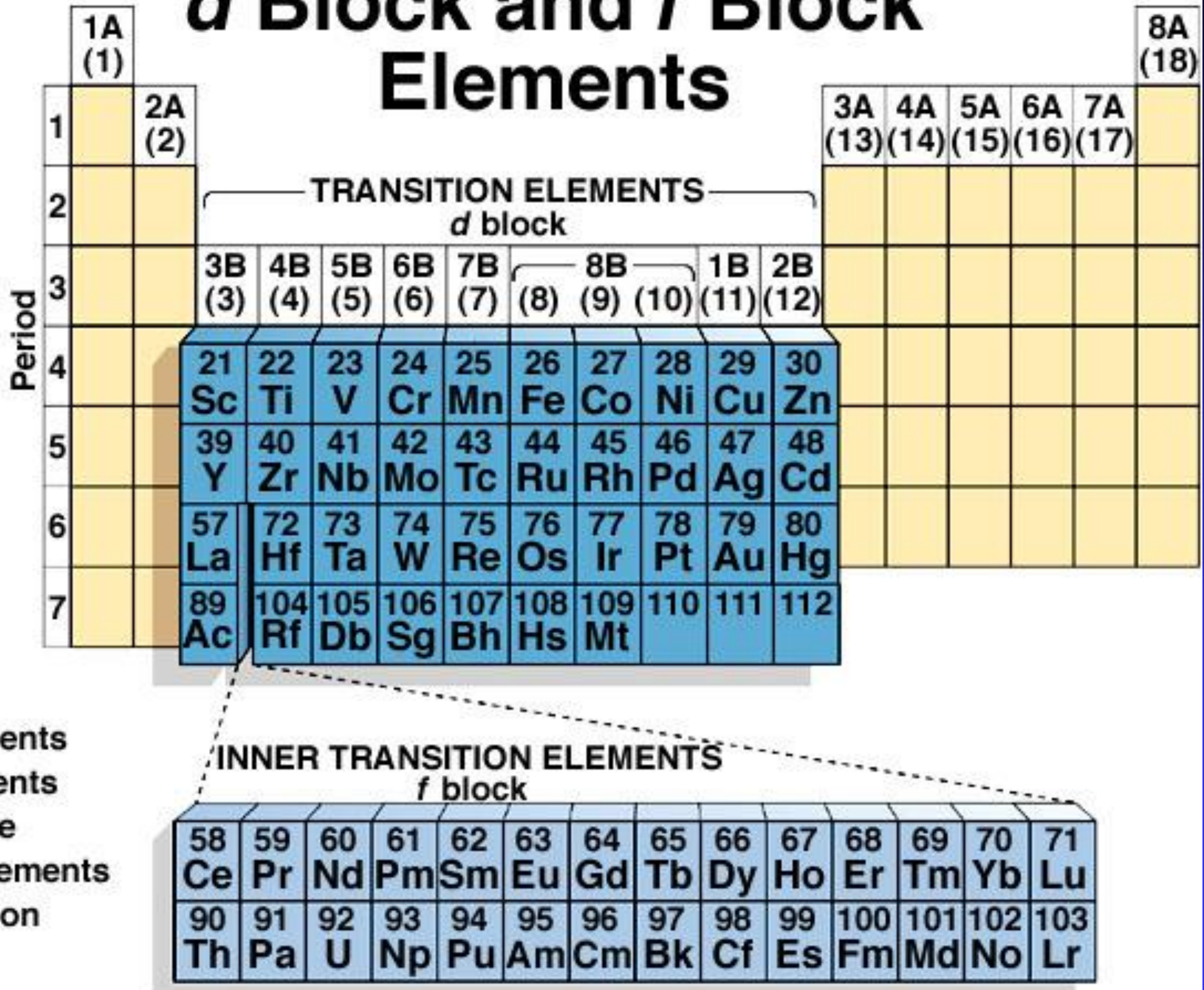
Transition Metals

Similarities within a given period

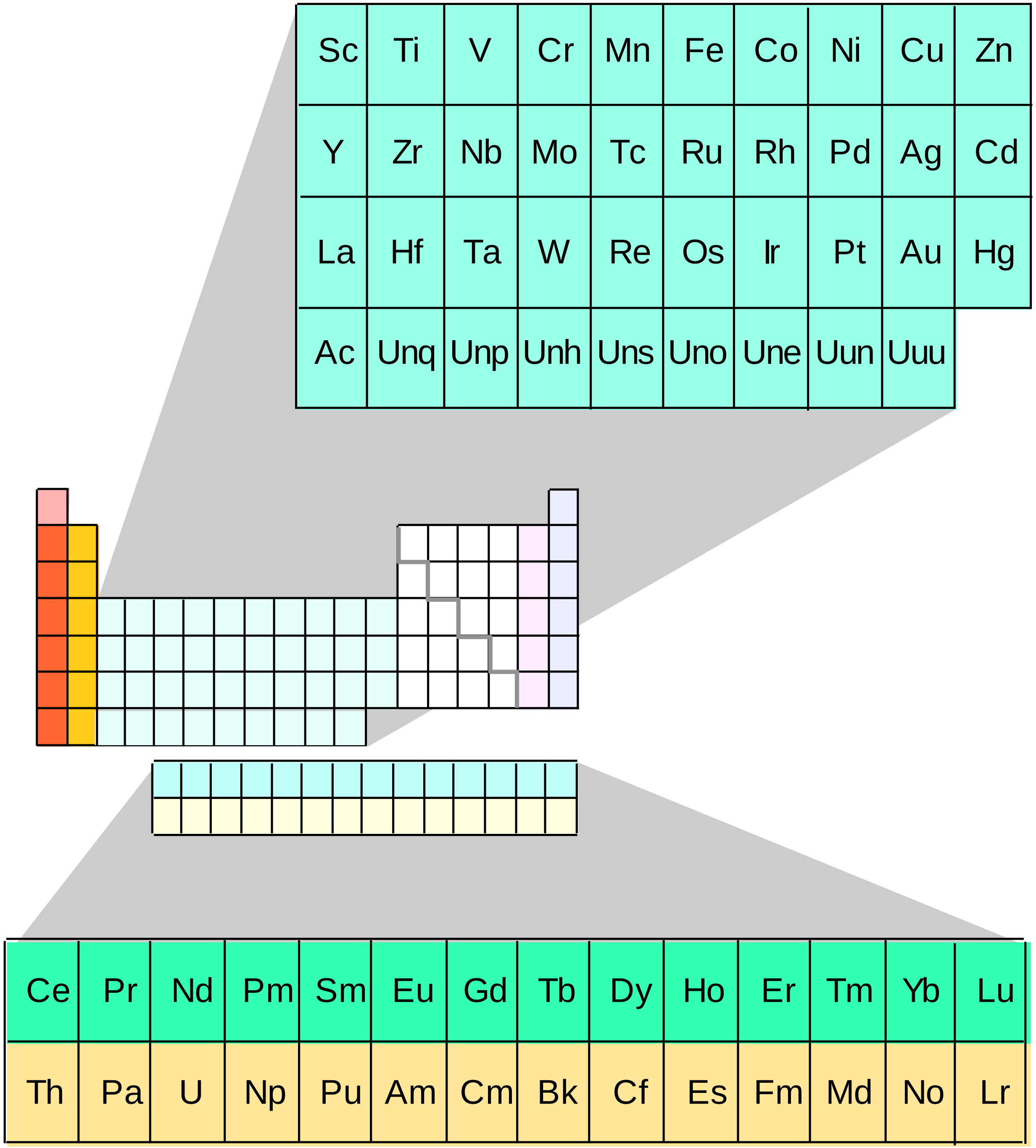
and within a given group.

Last electrons added are inner electrons (*d*’s, *f*’s).

d Block and *f* Block Elements



- *d* block elements
- *f* block elements
- Periodic table
- Transition elements
- Inner transition elements


Sc Ti V Cr Mn Fe Co Ni Cu Zn
Y Zr Nb Mo Tc Ru Rh Pd Ag Cd
La Hf Ta W Re Os Ir Pt Au Hg
Ac Unq Unp Unh Uns Uno Une Uun Uuu
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr

d-block transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac†	Unq	Unp	Unh	Uns	Uno	Une	Uun	Uuu	

f-block transition elements

*Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
† Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Period 4 Transition Metals

Titanium, Ti

Chromium, Cr

Scandium, Sc

Vanadium, V

Manganese, Mn

Cobalt, Co

Copper, Cu

Iron, Fe

Nickel, Ni

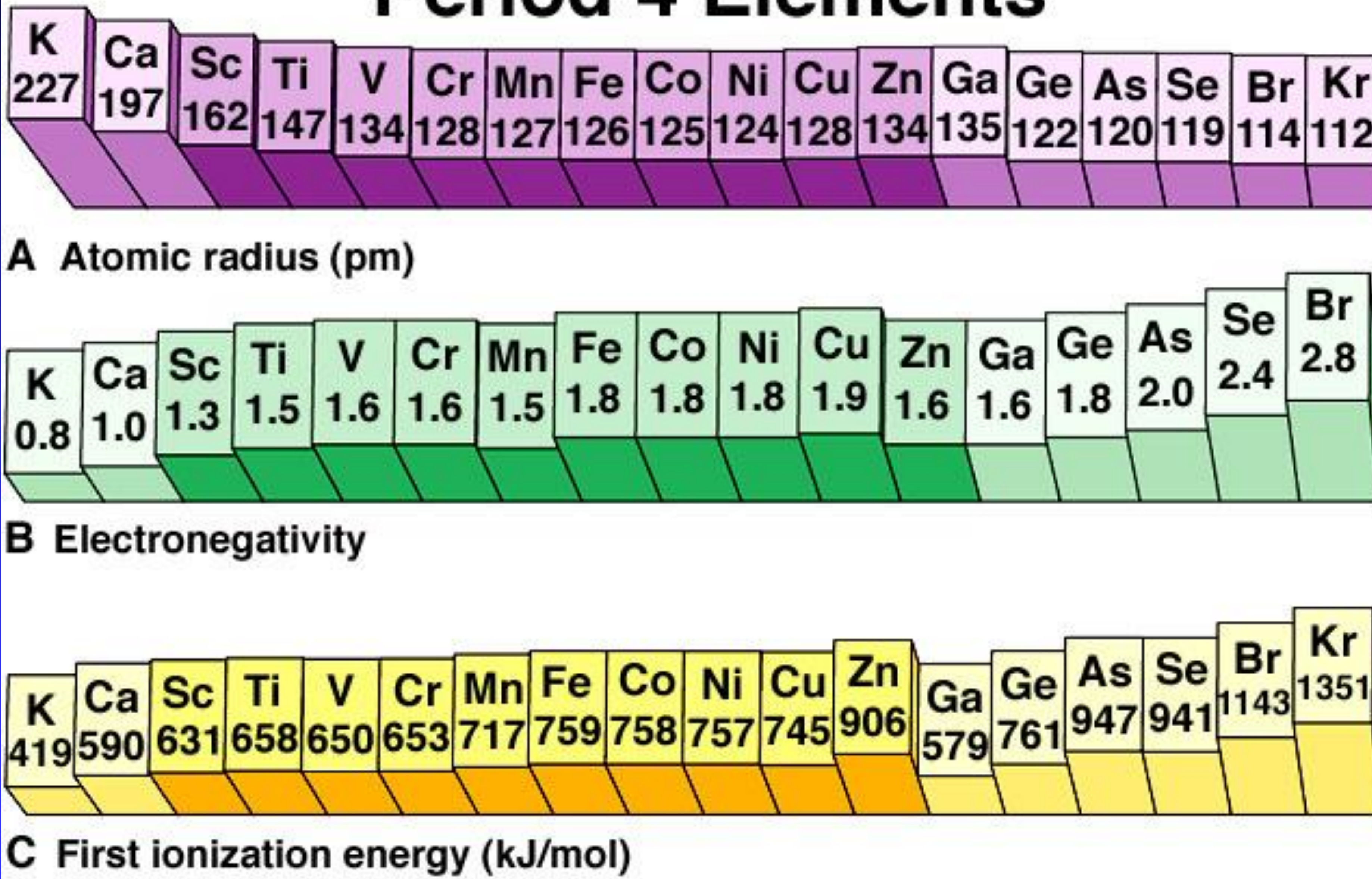
Zinc, Zn

Orbital Occupancy

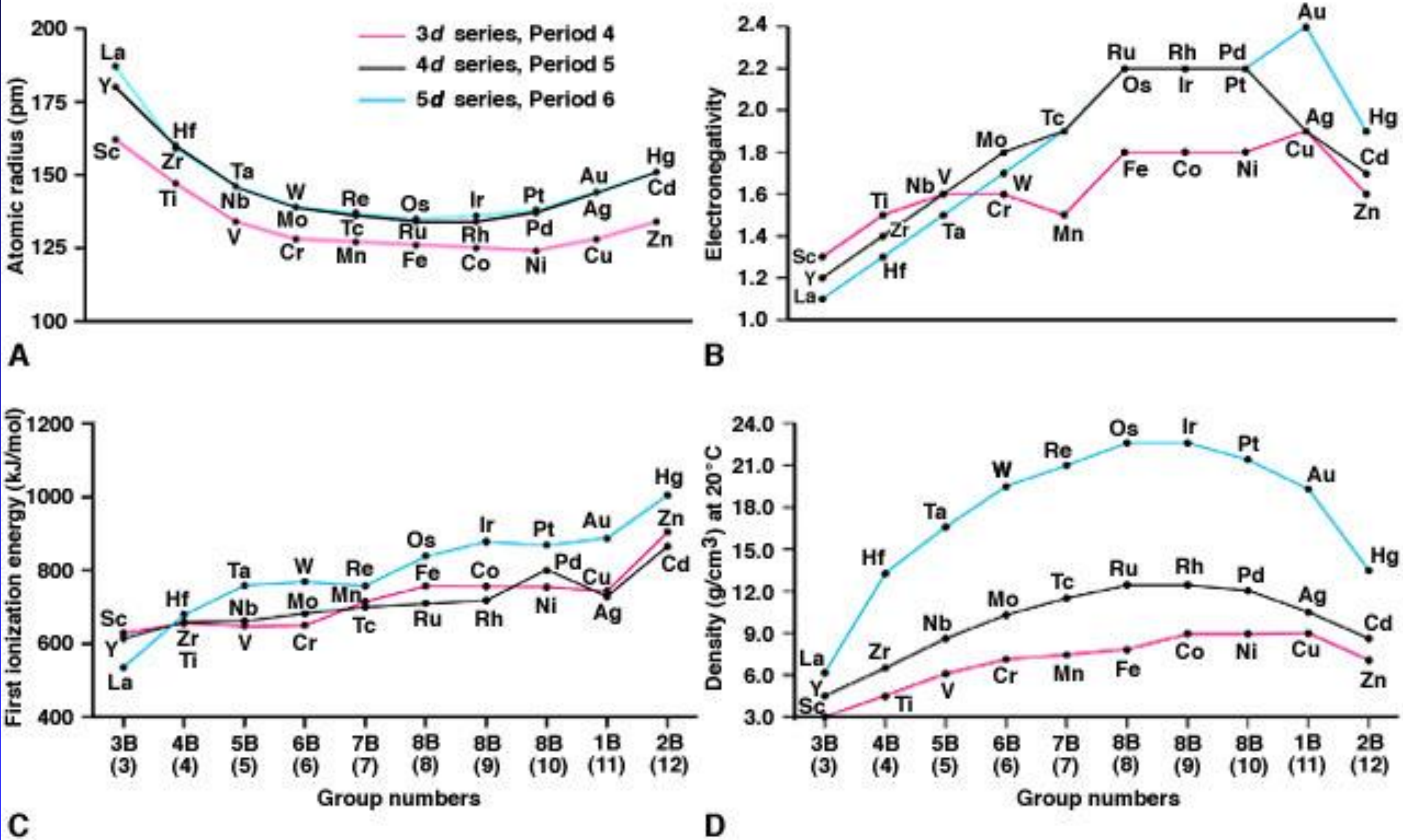
Table 23.1 Orbital Occupancy of the Period 4 Transition Metals

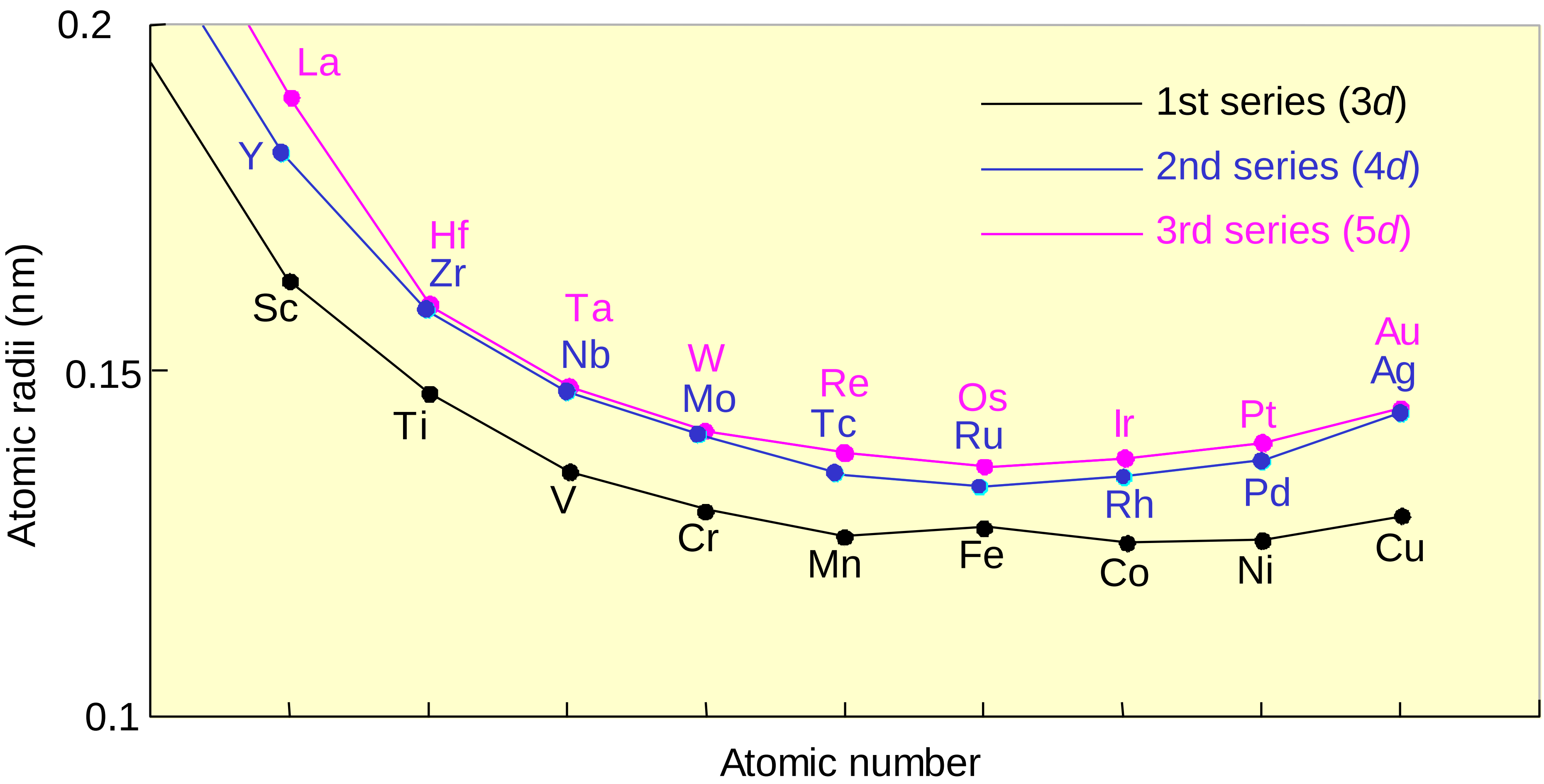
Element	Partial Orbital Diagram										Unpaired Electrons
	4*s*	3*d*					4*p*				
Sc	↑↓	↑									1
Ti	↑↓	↑	↑								2
V	↑↓	↑	↑	↑							3
Cr	↑	↑	↑	↑	↑	↑					6
Mn	↑↓	↑	↑	↑	↑	↑					5
Fe	↑↓	↑↓	↑	↑	↑	↑					4
Co	↑↓	↑↓	↑↓	↑	↑	↑					3
Ni	↑↓	↑↓	↑↓	↑↓	↑	↑					2
Cu	↑	↑↓	↑↓	↑↓	↑↓	↑↓					1
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓					0

Horizontal Trends in Period 4 Elements



Vertical Trends within the Transition Elements





0.2
0.15
0.1
Atomic radii (nm)
Atomic number
1st series (3*d*)
2nd series (4*d*)
3rd series (5*d*)
La
Y
Hf
Zr
Sc
Ta
Nb
Ti
W
Mo
V
Re
Tc
Cr
Os
Ru
Mn
Fe
Ir
Rh
Co
Pt
Pd
Ni
Au
Ag
Cu

Multiple Oxidation States

Oxidation States and *d*-Orbital Occupancy

Table 23.2 Oxidation States and *d*-Orbital Occupancy of the Period 4 Transition Metals*

Oxidation State	3B (3) Sc	4B (4) Ti	5B (5) V	6B (6) Cr	7B (7) Mn	8B (8) Fe	8B (9) Co	8B (10) Ni	1B (11) Cu	2B (12) Zn
0	0 (d^1)	0 (d^2)	0 (d^3)	0 (d^5)	0 (d^5)	0 (d^6)	0 (d^7)	0 (d^8)	0 (d^{10})	0 (d^{10})
+1			+1 (d^3)	+1 (d^5)	+1 (d^5)		+1 (d^7)	+1 (d^8)	+1 (d^{10})	
+2		+2 (d^2)	+2 (d^3)	**+2 (d^4)**	**+2 (d^5)**	**+2 (d^6)**	**+2 (d^7)**	**+2 (d^8)**	**+2 (d^9)**	**+2 (d^{10})**
+3	**+3 (d^0)**	+3 (d^1)	+3 (d^2)	**+3 (d^3)**	+3 (d^4)	**+3 (d^5)**	**+3 (d^6)**	+3 (d^7)	+3 (d^8)	
+4		**+4 (d^0)**	**+4 (d^1)**	+4 (d^2)	**+4 (d^3)**	+4 (d^4)	+4 (d^5)	+4 (d^6)		
+5			**+5 (d^0)**	+5 (d^1)	+5 (d^2)		+5 (d^4)			
+6				**+6 (d^0)**	+6 (d^1)	+6 (d^2)				
+7					**+7 (d^0)**					

*Most important in color.

Metallic Behavior/Reducing Strength

Lower oxidation state = more metallic

Standard Electrode Potentials

Table 23.3 Standard Electrode Potentials of Period 4 M^{2+} Ions

Half-Reaction			E^0 (V)
$Ti^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Ti(s)$	–1.63
$V^{2+}(aq))2e^-$	$\rightleftharpoons$	$V(s)$	–1.19
$Cr^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Cr(s)$	–0.91
$Mn^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Mn(s)$	–1.18
$Fe^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Fe(s)$	–0.44
$Co^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Co(s)$	–0.28
$Ni^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Ni(s)$	–0.25
$Cu^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Cu(s)$	0.34
$Zn^{2+}(aq)+2e^-$	$\rightleftharpoons$	$Zn(s)$	–0.76

Color and Magnetism

Colors of Period 4 Transition Metals

e^- in partially filled d sublevel absorbs visible light moves to slightly higher energy d orbital

Magnetic properties due to unpaired electrons

Properties of Group 6 B (6) Elements

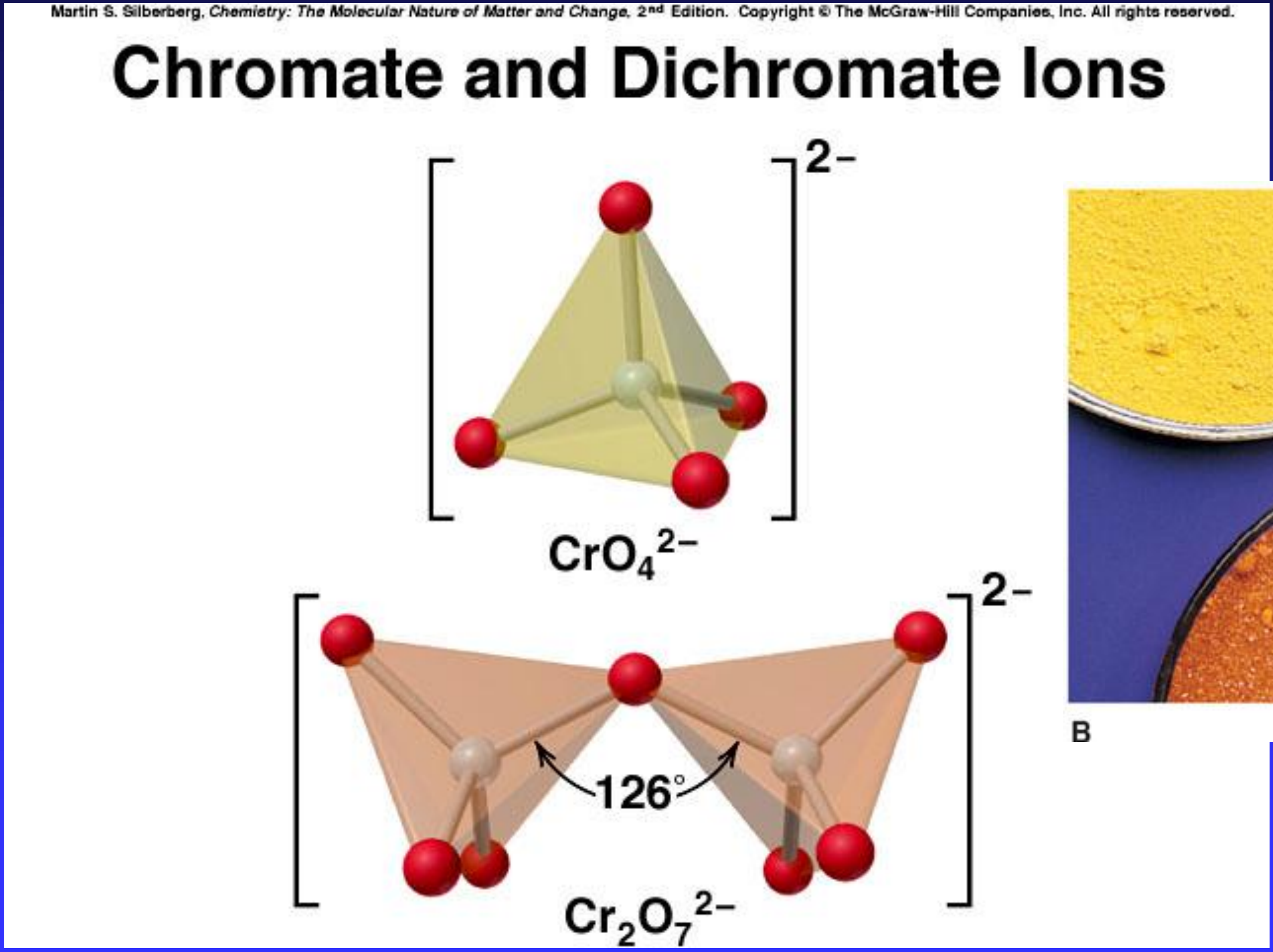
Table 23.4 Some Properties of Group 6B(6) Elements

Elements	Atomic Radius (pm)	IE_1(kJ/mol)	E^0(V) for $M^{3+}(aq)|M(s)$
Cr	128	653	−0.74
Mo	139	685	−0.20
W	139	770	−0.11

Electronegativity increases down column

Chromium

Chemical properties reflect oxidation state



B

Valence-State Electronegativity

Electronegativity, EN:

electron "pulling power"

Valence-state EN:

metal in higher oxidation state

is more positive

has stronger pull on electrons

is more electronegative

"Effective EN"

Manganese

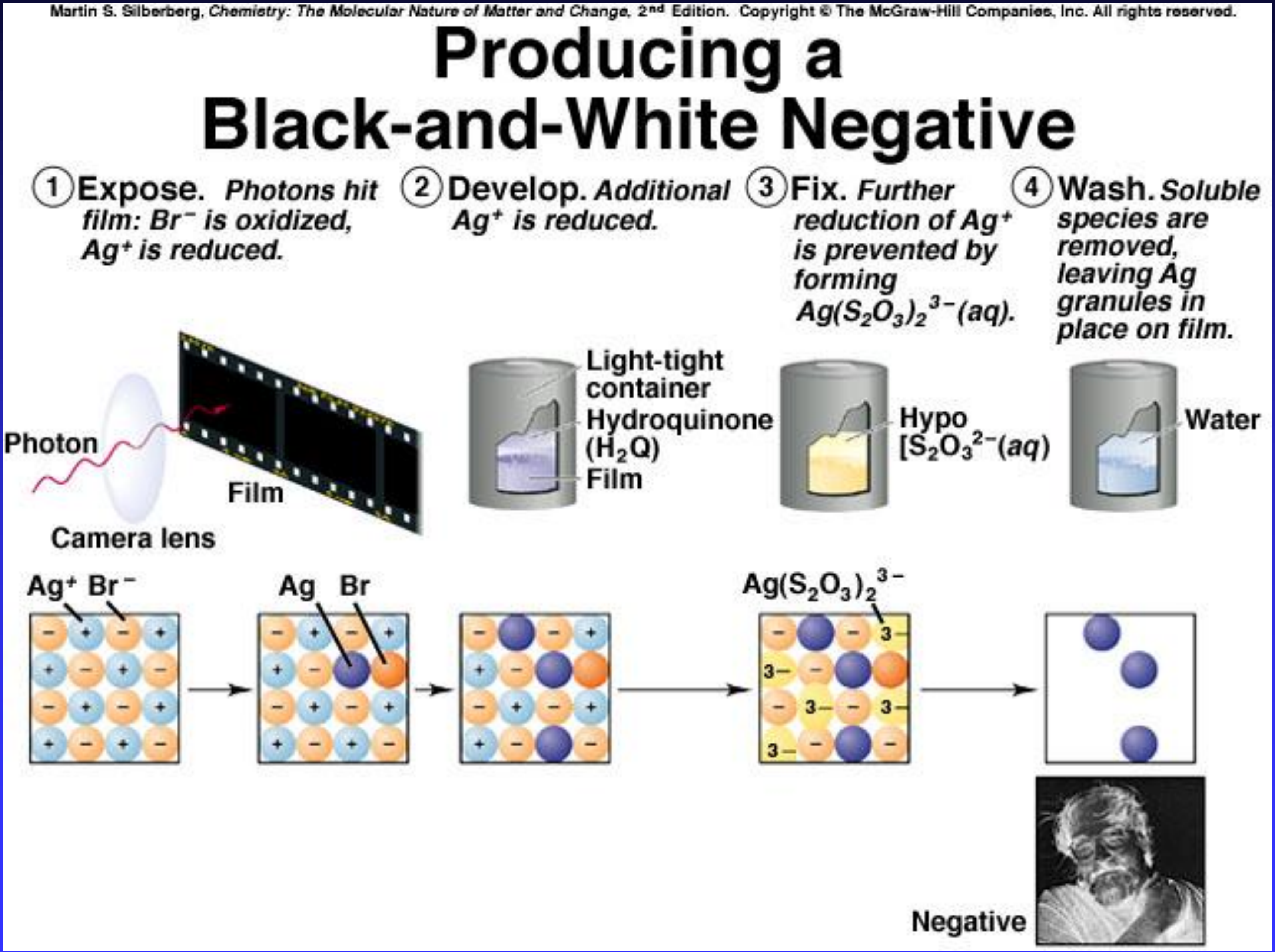
Oxidation States of Manganese

Table 23.5 Some Oxidation States of Manganese

Oxidation state*	**Mn(II)**	Mn(III)	**Mn(IV)**	Mn(VI)	**Mn(VII)**
Example	Mn^{2+}	Mn_2O_3	MnO_2	MnO_4^{2-}	Mno_4^-
Ion configuration	d^5	d^4	d^3	d^1	d^0
Oxide acidity	BASIC				ACIDIC

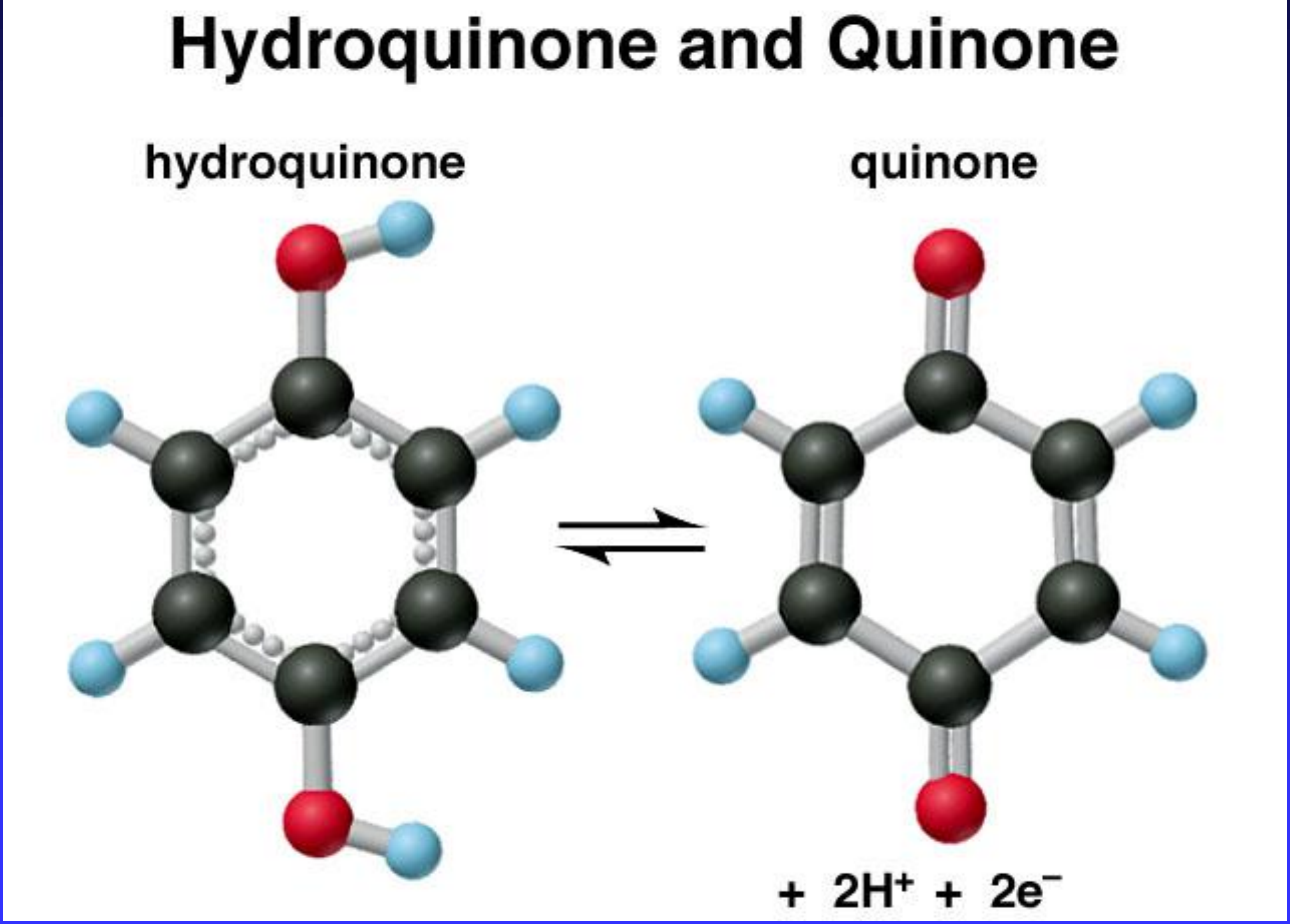
*Most common states in boldface.

Silver



Martin S. Silberberg, Chemistry: The Molecular Nature of Matter and Change, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.
Producing a Black-and-White Negative
① Expose. Photons hit film: Br^- is oxidized, Ag^+ is reduced.
② Develop. Additional Ag^+ is reduced.
③ Fix. Further reduction of Ag^+ is prevented by forming $Ag(S_2O_3)_2^{3-}(aq)$.
④ Wash. Soluble species are removed, leaving Ag granules in place on film.
Photon
Camera lens
Film
Light-tight container
Hydroquinone (H_2Q)
Film
Hypo [$S_2O_3^{2-}(aq)$]
Water
Ag^+ Br^-
Ag Br
$Ag(S_2O_3)_2^{3-}$
Negative

Weak Reducing Agent, H_2Q



Mercury

Coordination Compound

Consist of a complex ion and necessary counter ions

$[Co(NH_3)_5Cl]Cl_2$

Complex ion: $[Co(NH_3)_5Cl]^{2+}$

Co^{3+} + $5\ NH_3$ + Cl^-

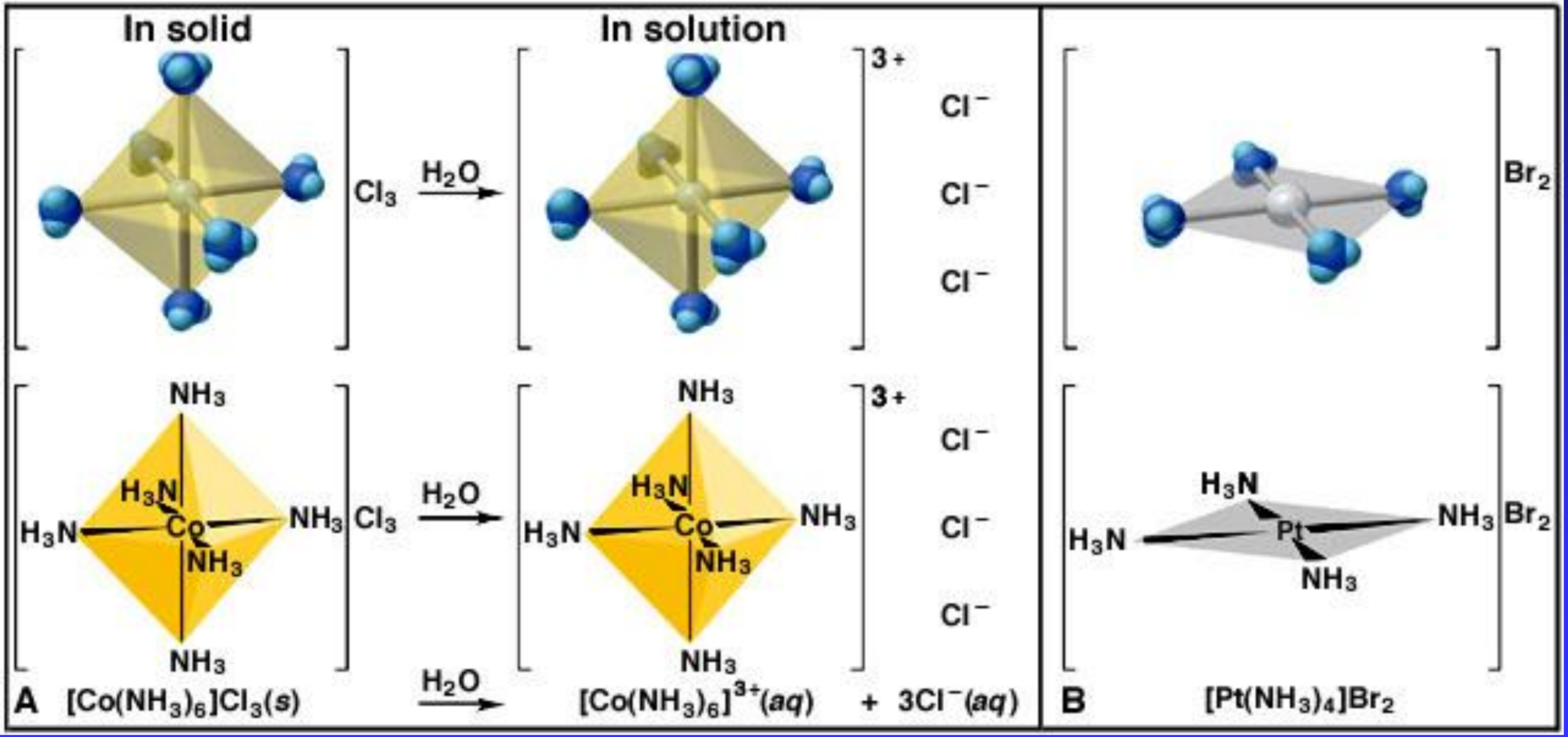
= 1(3+) + 5 (0) + 1(1-)

= 2+

Counter ions: $2\ Cl^-$

Components of a Coordination Compound

$[Co(NH_3)_6]Cl_3$ $[Pt(NH_3)_4]Br_2$



Complex ion remains intact upon dissolution in water

Complex Ion

Species where transition metal ion is surrounded by a certain number of ligands.

Transition metal ion: Lewis acid

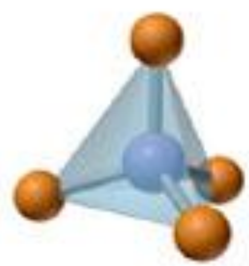
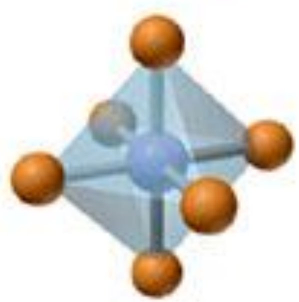
Ligands: Lewis bases

$Co(NH_3)_6^{3+}$

$Pt(NH_3)_3Br^+$

Complex Ions: Coordination Numbers, Shapes

Table 23.6 Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape		Examples
2	Linear		$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square planar		$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4	Tetrahedral		$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6	Octahedral		$[Ti(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cr(NH_3)_4CL_2]^+$, $[Mn(H_2O)_6]^{2+}$, $[FeCl_6]^{3-}$, $[Co(en)_3]^{3+}$

Ligands

Molecule or ion having a lone electron pair that can be used to form a bond to a metal ion (Lewis base).

coordinate covalent bond: metal-ligand bond

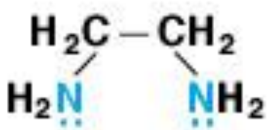
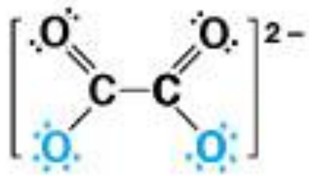
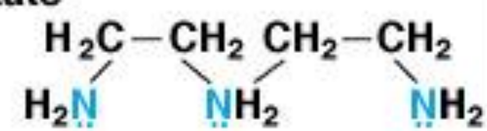
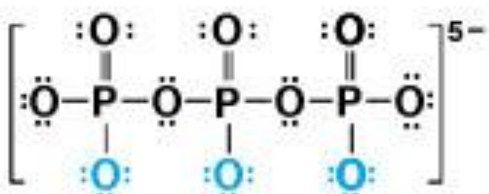
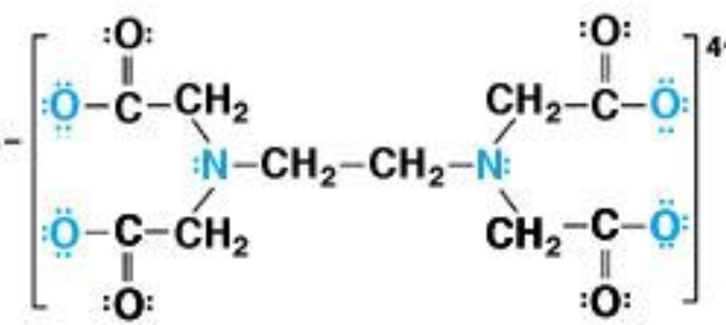
monodentate: one bond to metal ion

bidentate: two bond to metal ion

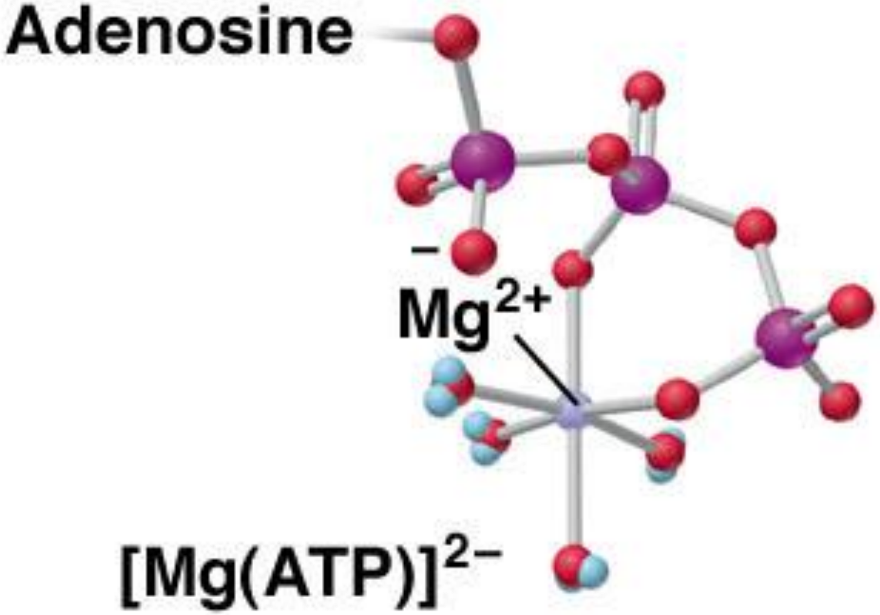
polydentate: more than two bonds to a metal ion possible

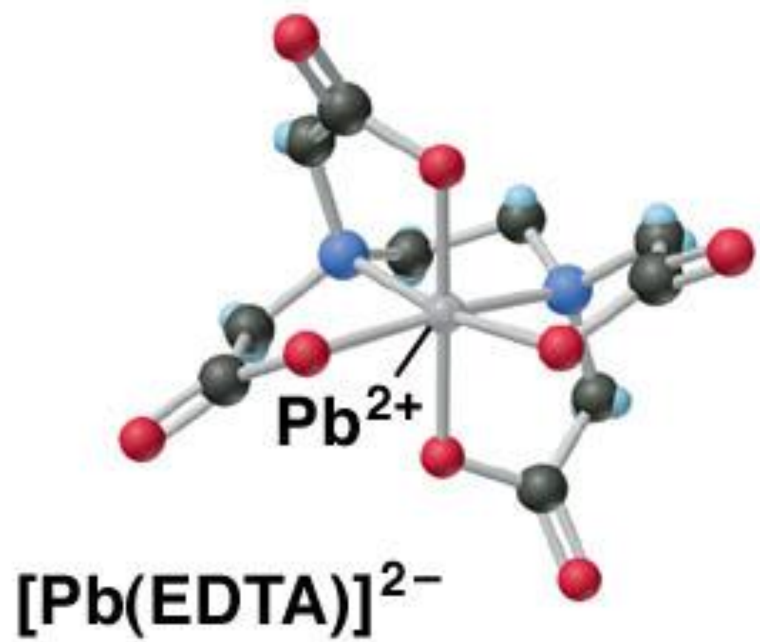
Ligands in Coordination Compounds

Table 23.7 Some Common Ligands in Coordination Compounds

Ligand Type	Examples
Unidentate	$H_2\ddot{O}:$ water; $:\ddot{F}:^-$ fluoride ion; $[:C\equiv N:]^-$ cyanide ion; $[:\ddot{O}-H]^-$ hydroxide ion; $:NH_3$ ammonia; $:\ddot{Cl}:^-$ chloride ion; $[:\ddot{S}=C=\ddot{N}:]^-$ (S or N) thiocyanate ion; $[:\ddot{O}-N=\ddot{O}:]^-$ (O or N) nitrite ion
Bidentate	 ethylenediamine (en);  oxalate ion
Polydentate	 diethylenetriamine;  triphosphate ion;  ethylenediaminetetraacetate (EDTA) ion

Grabbing Ions





Formulas of Coordination Compounds

1. Cation then anion
2. Total charges must balance to zero
3. Complex ion in brackets

$$K_2[Co(NH_3)_2Cl_4]$$

$$[Co(NH_3)_4Cl_2]Cl$$

Names of Coordination Compounds

1. **Cation then anion**
2. **Ligands**

    in alphabetical order before metal ion

    neutral: molecule name*

    anionic: -ide → -o

    prefix indicates number of each

3. **Oxidation state** of metal ion in () only if more than one possible

4. If complex ion = anion, metal ending → -ate

Names of Some Ligands

Table 23.8 Names of Some Neutral and Anionic Ligands

Name	Formula
A. Neutral	
Aqua	H_2O
Ammine	NH_3
Carbonyl	CO
Nitrosyl	NO
B. Anionic	
Fluoro	F^-
Chloro	Cl^-
Bromo	Br^-
Iodo	I^-
Hydroxo	OH^-
Cyano	CN^-

Metal Ions in Complex Anions

Table 23.9 Names of Some Metal Ions in Complex Anions

Metal	Name in Anion
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

Examples

$K_2[Co(NH_3)_2Cl_4]$

potassium diamminetetrachlorocobaltate(II)

$[Co(NH_3)_4Cl_2]Cl$

tetraamminedichlorocobalt(III) chloride

Alfred Werner and Coordination Compounds

Table 23.10 Some Coordination Compounds of Cobalt Studied by Werner

Traditional Formula	Total Ions (Werner's Data*)	Free Cl^- (Werner's Data*)	Modern Formula	Charge of Complex Ion
$CoCl_3 \cdot 6NH_3$	4	3	$[Co(NH_3)_6]Cl_3$	3+
$CoCl_3 \cdot 5NH_3$	3	2	$[Co(NH_3)_5Cl]Cl_2$	2+
$CoCl_3 \cdot 4NH_3$	2	1	$[Co(NH_3)_4Cl_2]Cl$	1+
$CoCl_3 \cdot 3NH_3$	0	0	$[Co(NH_3)_3Cl_3]$	—

*Moles per mole of compound.

Isomerism in Coordination Compounds

ISOMERS

Same formula, different atom arrangement

Constitutional (structural) isomers

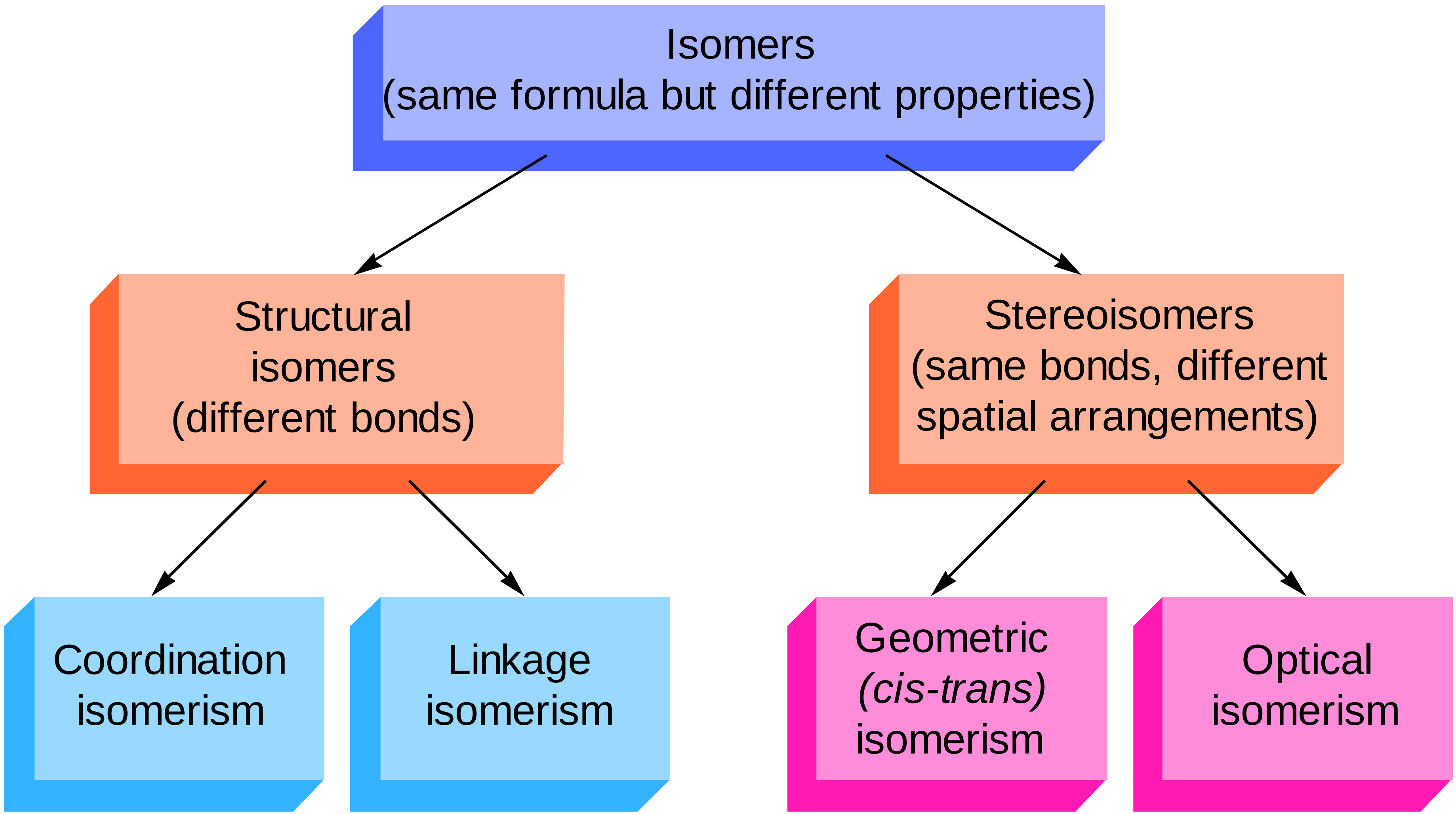
Atoms connected differently

- **Coordination isomers**: Ligand and counter-ion exchange
- **Linkage isomers**: Different donar atom

Stereoisomers

Different spatial arrangement

- **Geometric (*cis-trans*) isomers (diastereomers)**: Different arrangement around metal ion
- **Optical isomers (enantiomers)**: Nonsuperimposable mirror images



Isomers
(same formula but different properties)
Structural isomers (different bonds)
Stereoisomers (same bonds, different spatial arrangements)
Coordination isomerism
Linkage isomerism
Geometric *(cis-trans)* isomerism
Optical isomerism

Structural Isomerism 1

Coordination isomerism:

Composition of the complex ion varies.

$[Cr(NH_3)_5SO_4]Br$

and $[Cr(NH_3)_5Br]SO_4$

Structural Isomerism 2

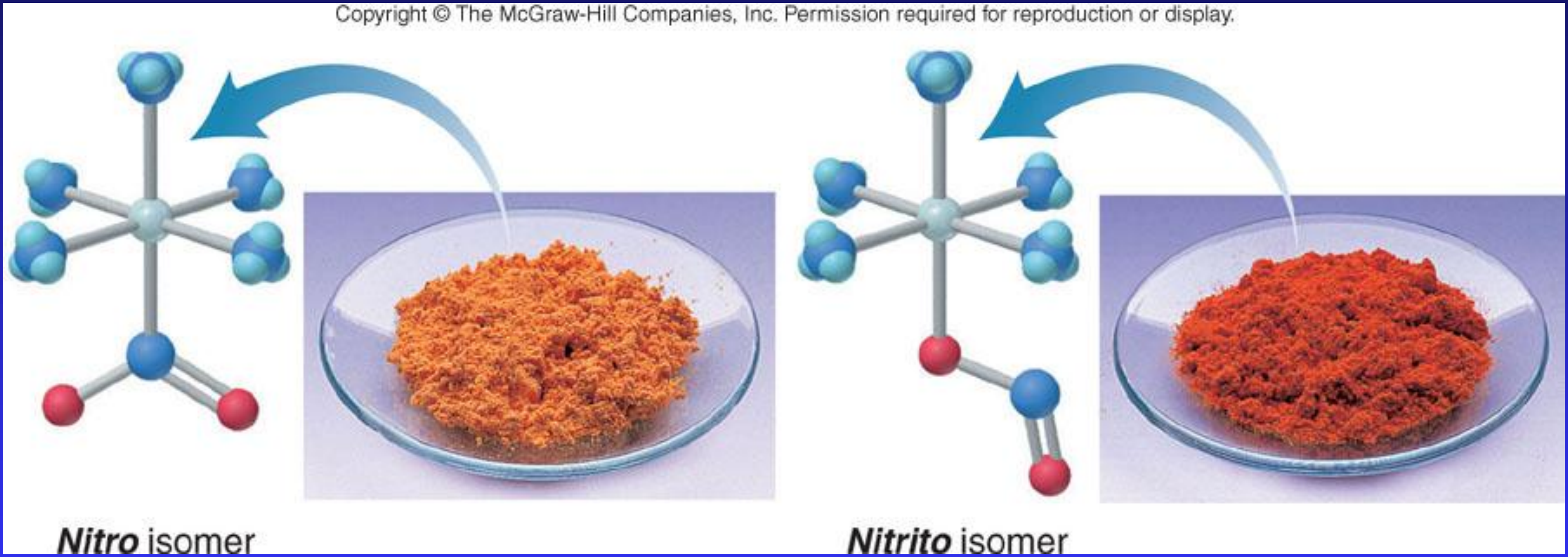
Ligand isomerism:

Same complex ion structure but point of attachment of at least one of the ligands differs.

$[Co(NH_3)_4(NO_2)Cl]Cl$

and $[Co(NH_3)_4(ONO)Cl]Cl$

Linkage Isomers



$[Co(NH_3)_5(NO_2)]Cl_2$
Pentaamminenitrocobalt(III) chloride

$[Co(NH_3)_5(ONO)]Cl_2$
Pentaamminenitritocobalt(III) chloride

Stereoisomerism 1

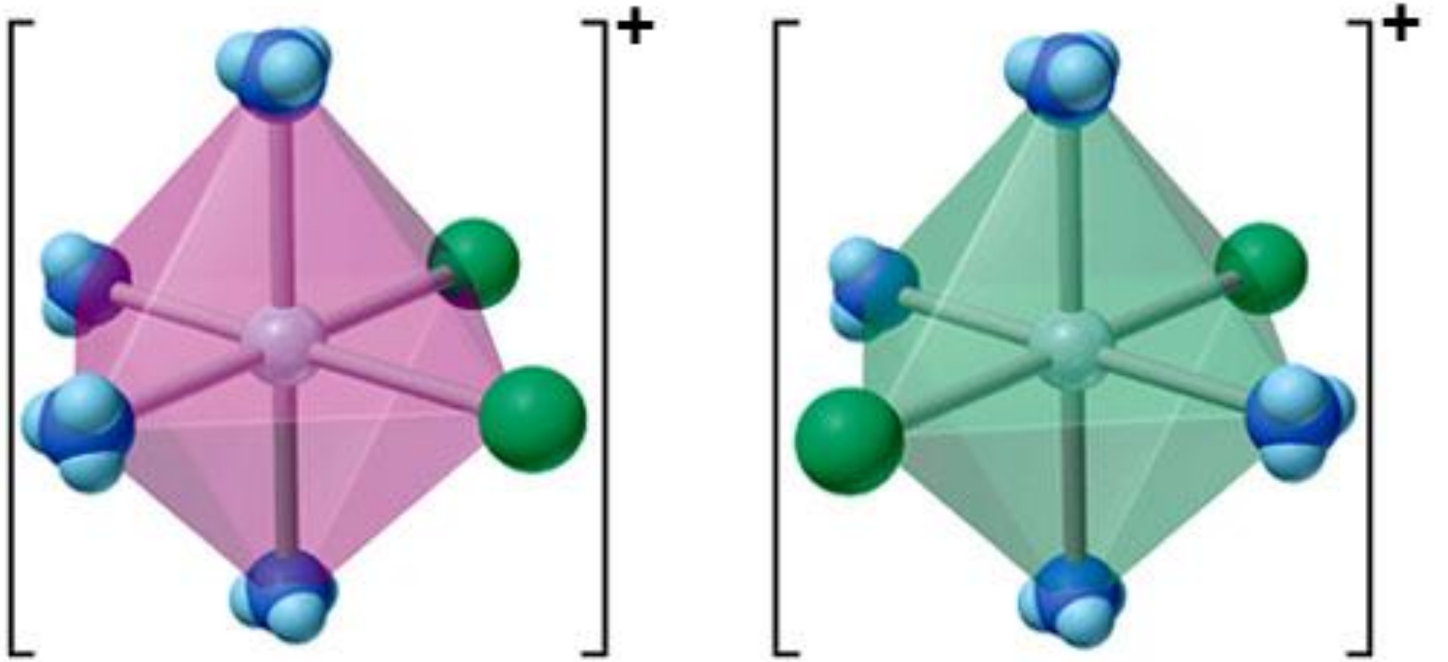
Geometric isomerism (cis-trans):

Atoms or groups arranged differently spatially relative to metal ion

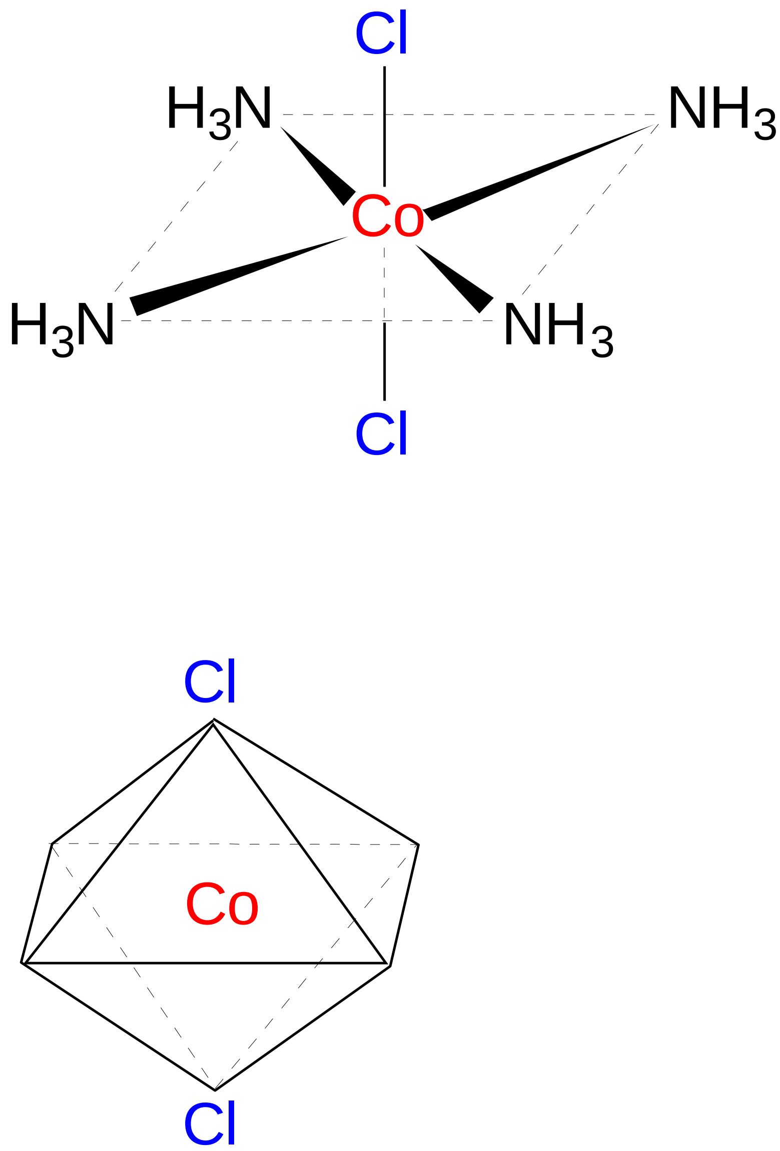
$Pt(NH_3)_2Cl_2$

Geometric (*cis-trans*) Isomerism

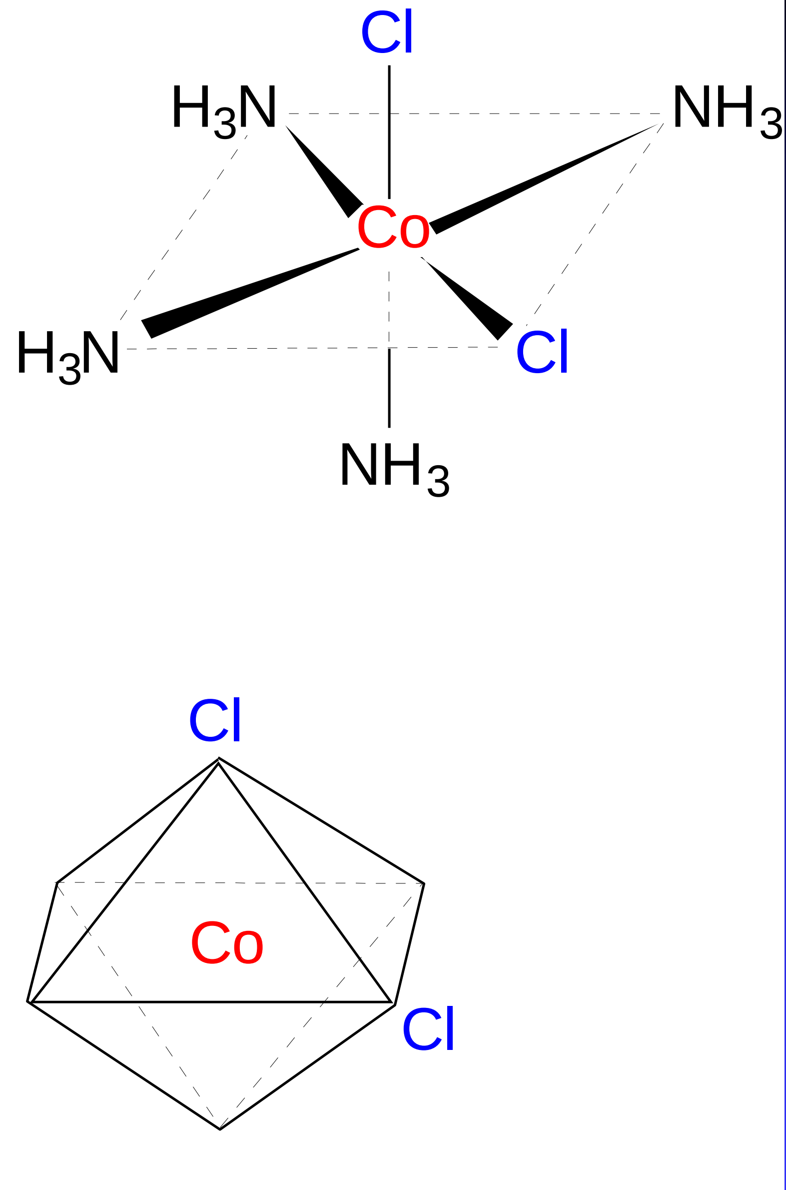
A *cis*–$[Pt(NH_3)_2Cl_2]$ *trans*–$[Pt(NH_3)_2Cl_2]$



B *cis*–$[Co(NH_3)_4Cl_2]^+$ *trans*–$[Co(NH_3)_4Cl_2]^+$



(a)

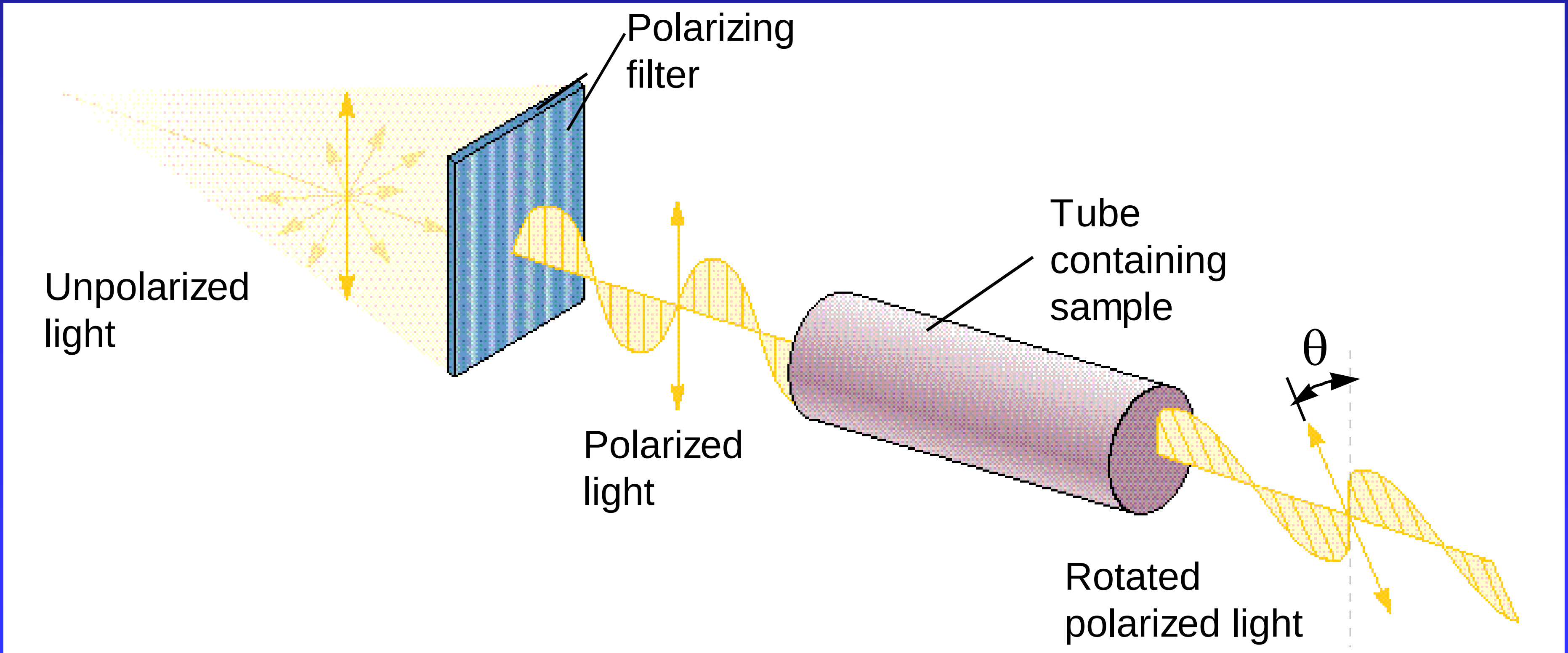


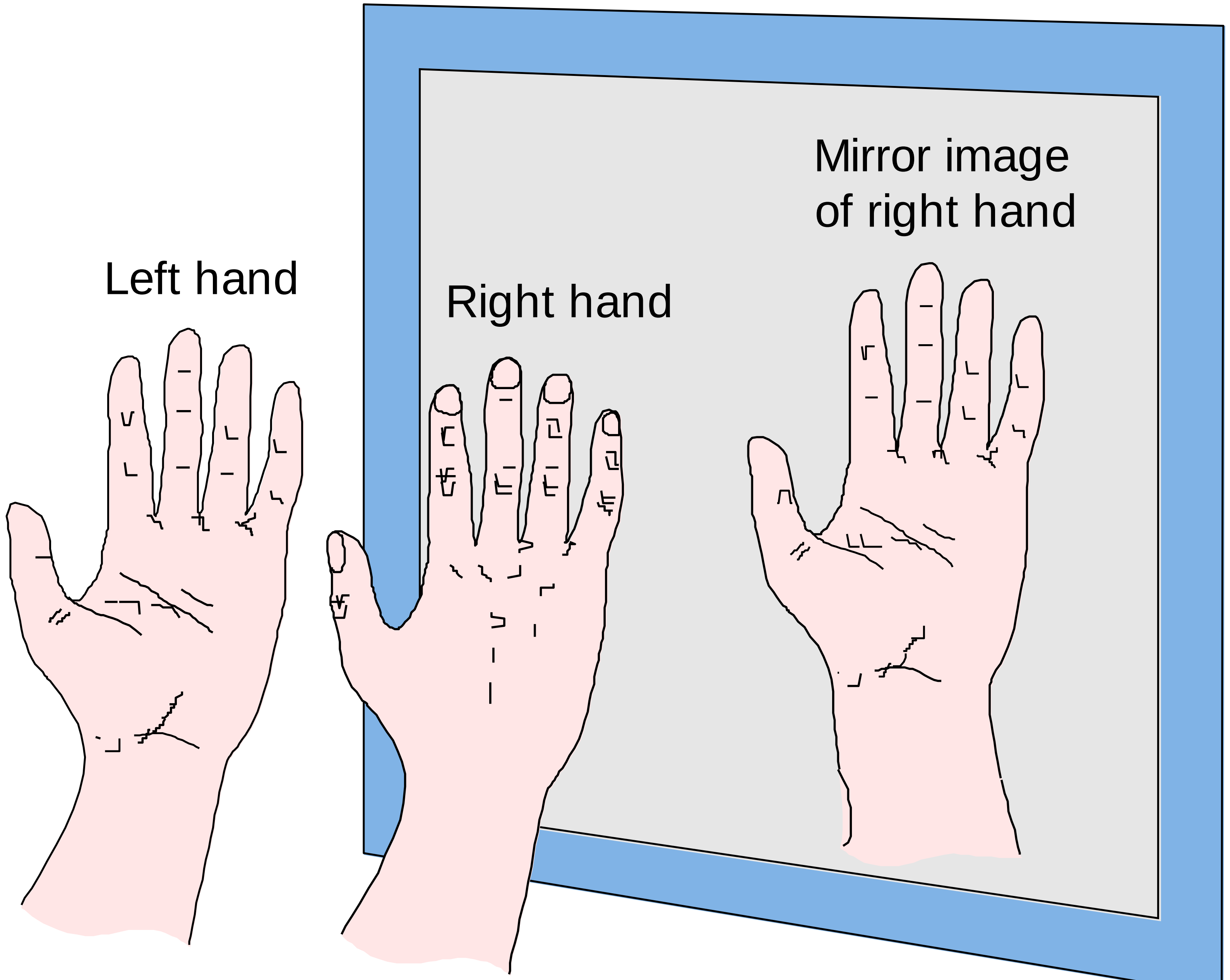
(b)

Stereoisomerism 2

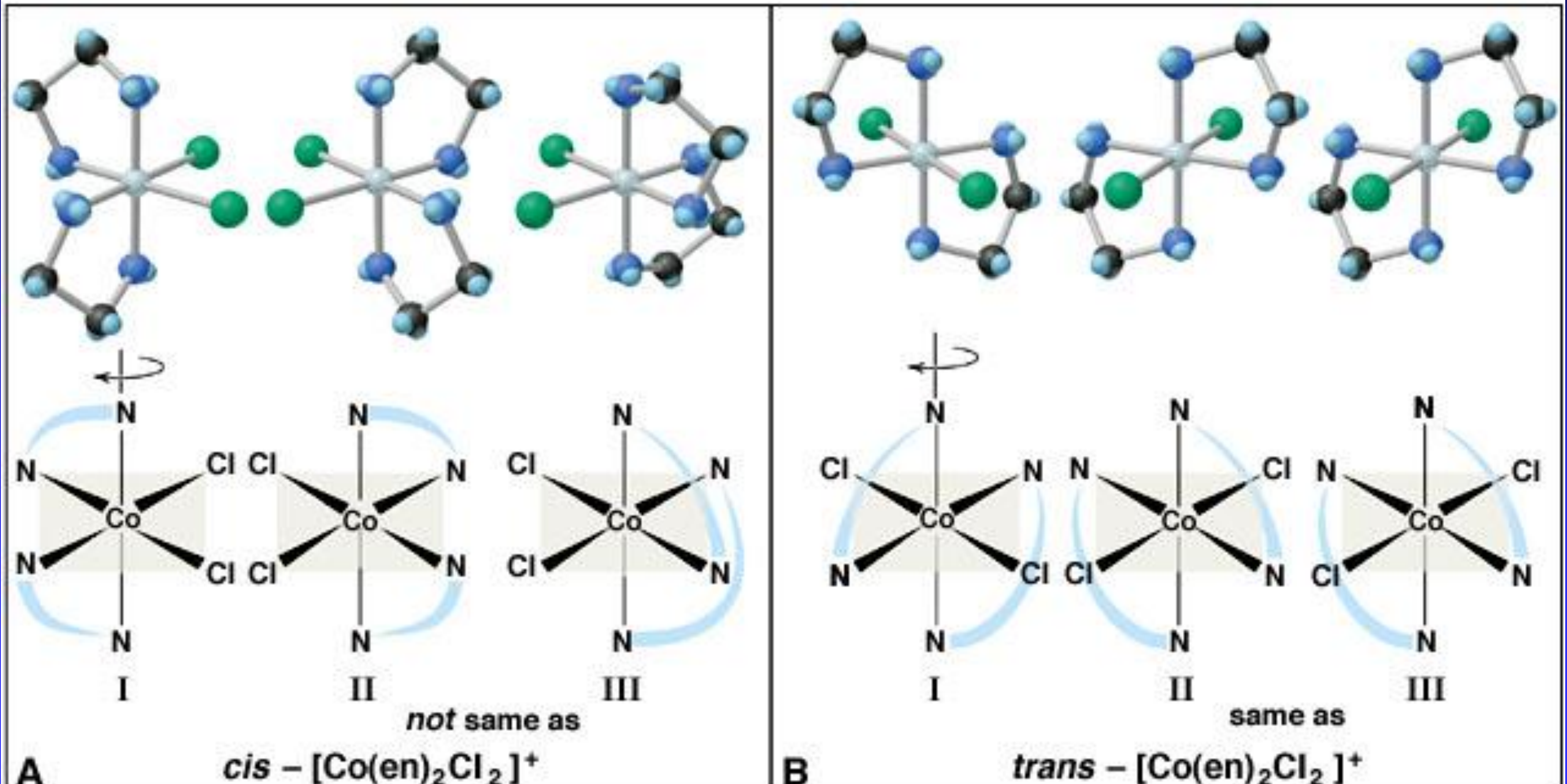
Optical isomerism:

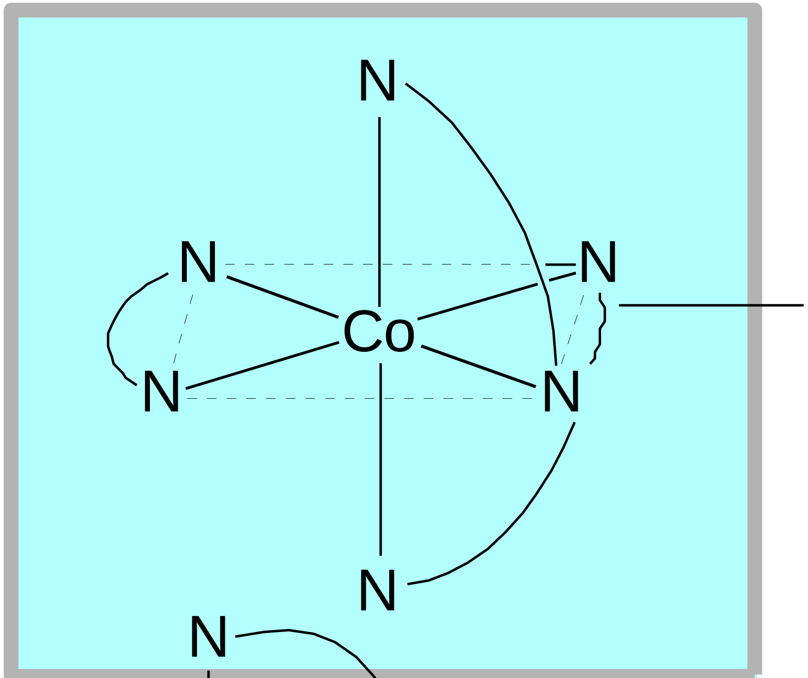
Have opposite effects on plane-polarized light (no superimposable mirror images)



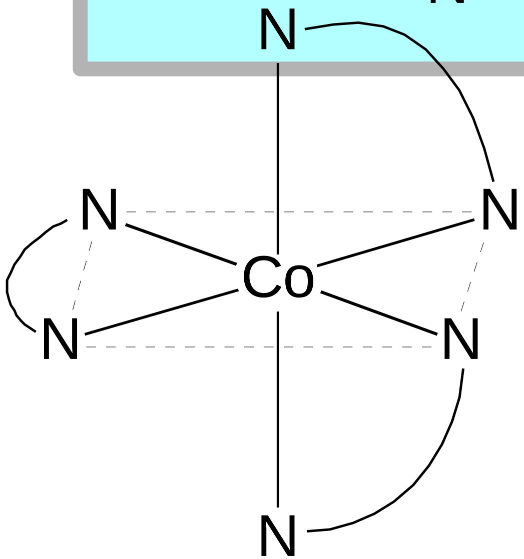

Left hand
Right hand
Mirror image
of right hand

Optical Isomerism in an Octahedral Complex Ion

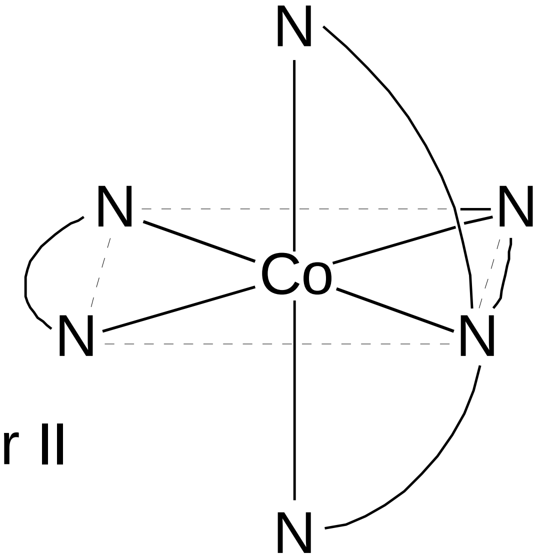




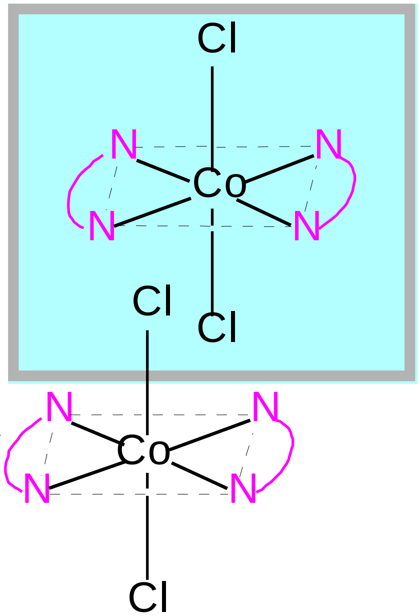
Mirror image of Isomer I



Isomer I



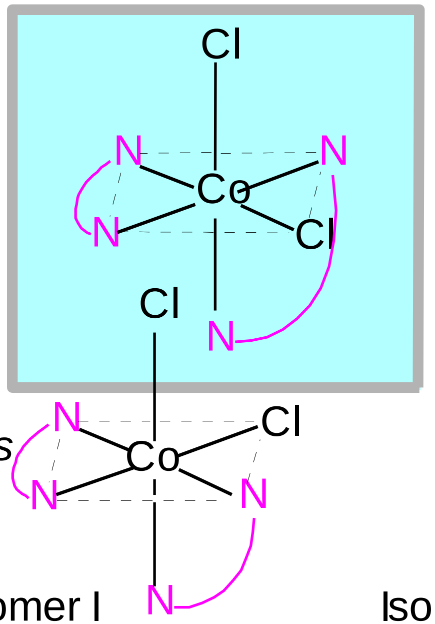
Isomer II



trans

The *trans* isomer and its mirror image are identical. They are not isomers of each other.

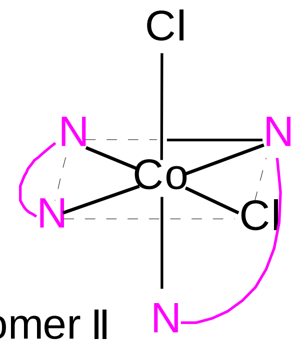
(a)



cis

Isomer I

Isomer II cannot be superimposed exactly on isomer I. They are not identical structures.

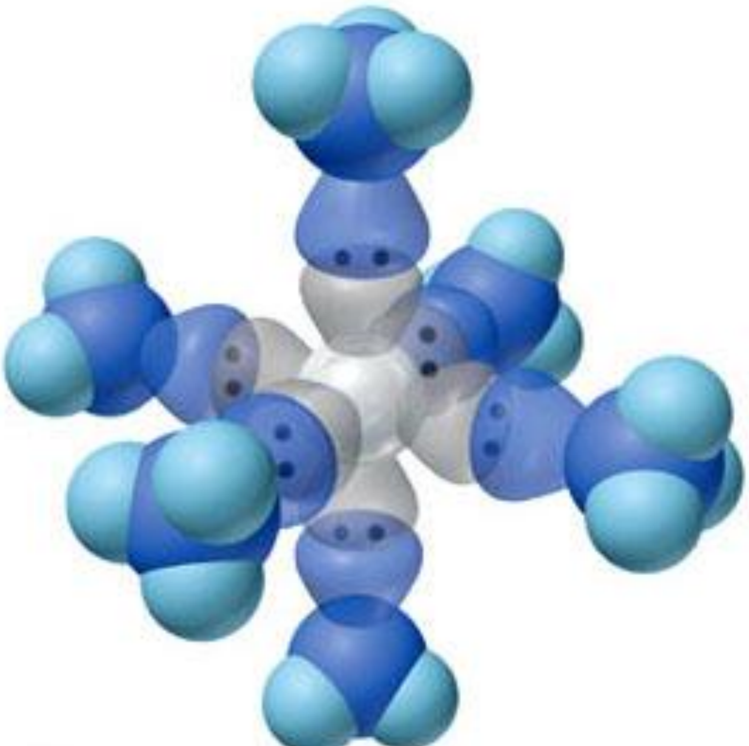


Isomer II

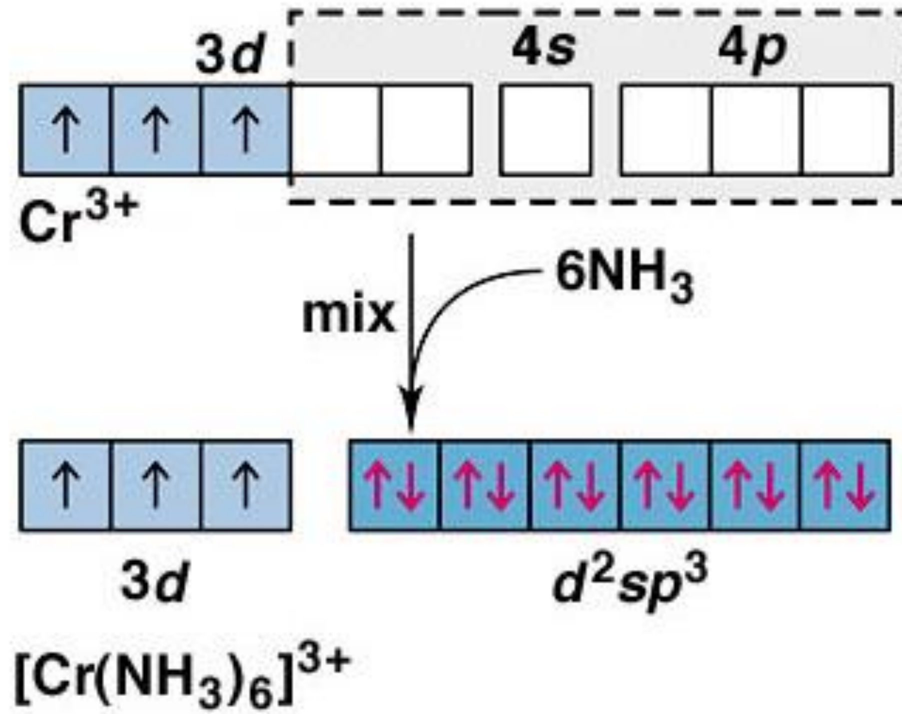
Isomer II has the same structure as the mirror image of isomer I.

(b)

Hybrid Orbitals and Bonding in an Octahedral Ion



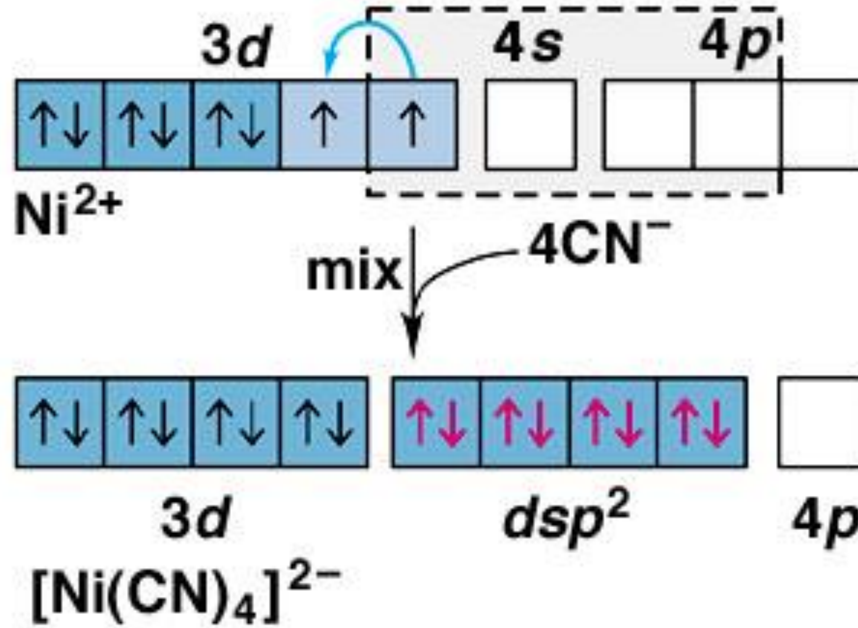
A



B

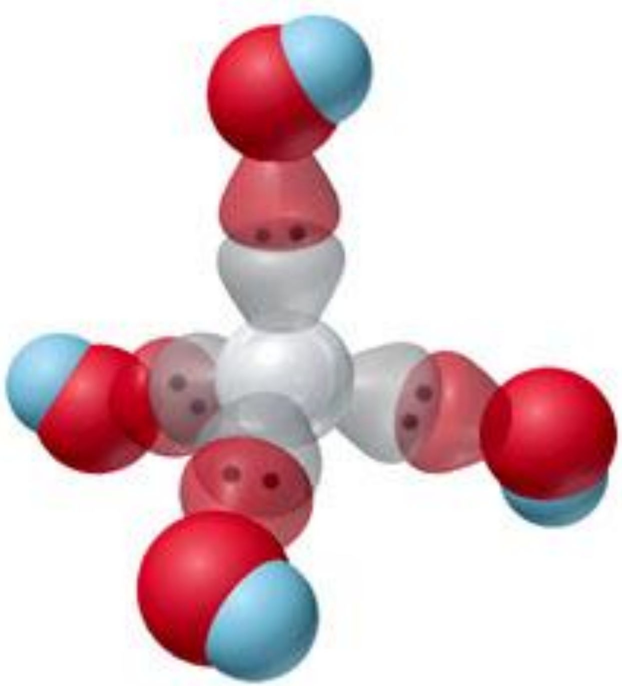
Hybrid Orbitals and Bonding in a Square Planar Ion

A

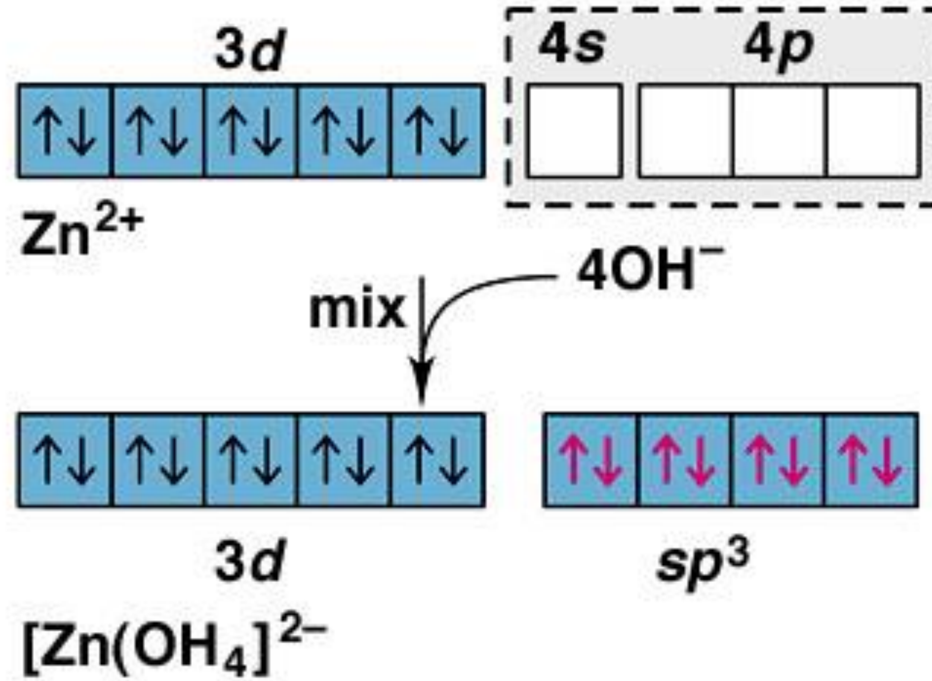


B

Hybrid Orbitals and Bonding in a Tetrahedral Ion



A



B

Crystal Field Theory

Focus: energies of the *d* orbitals

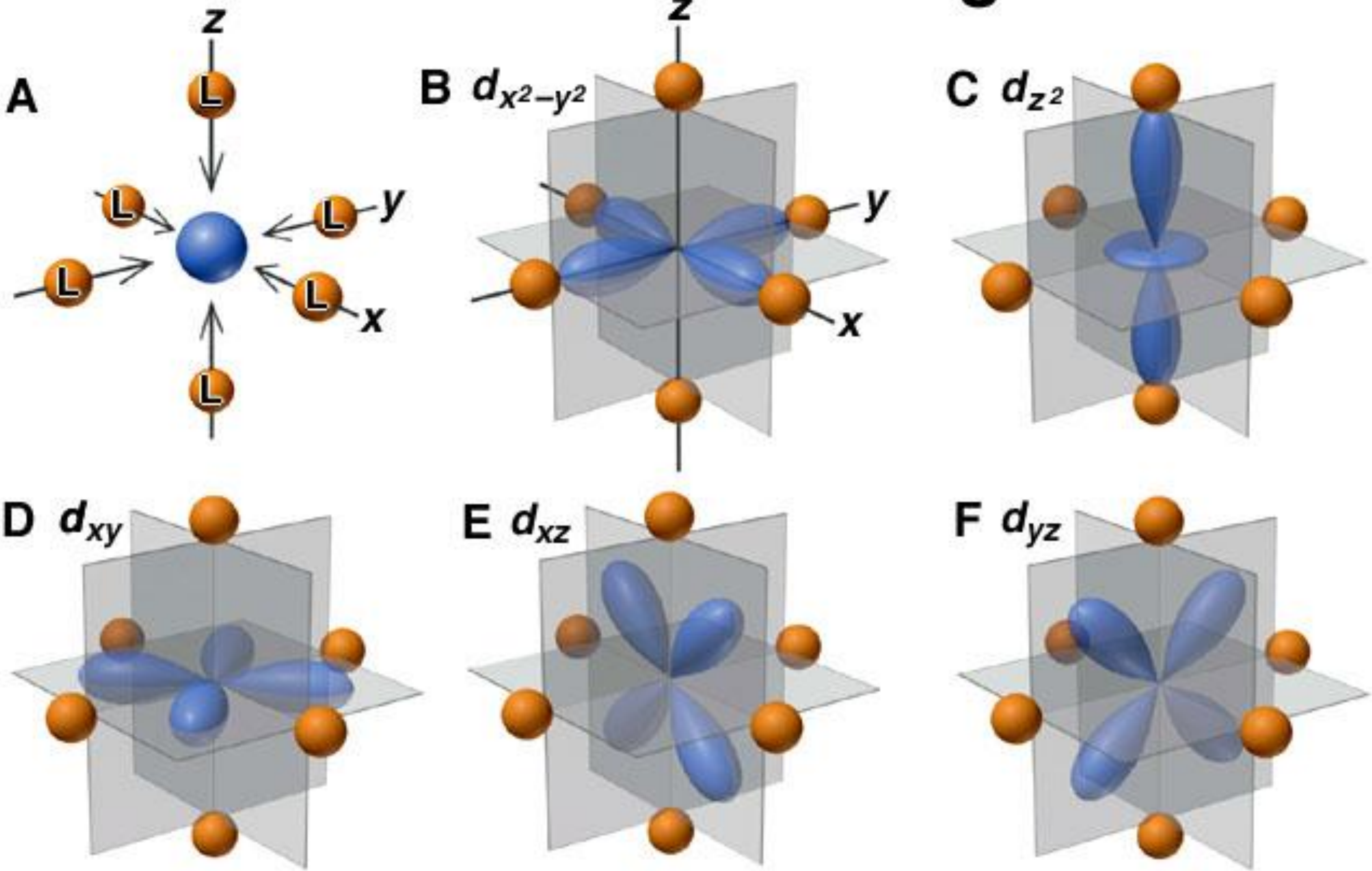
Assumptions

1. Ligands: negative point charges
2. Metal-ligand bonding: entirely ionic

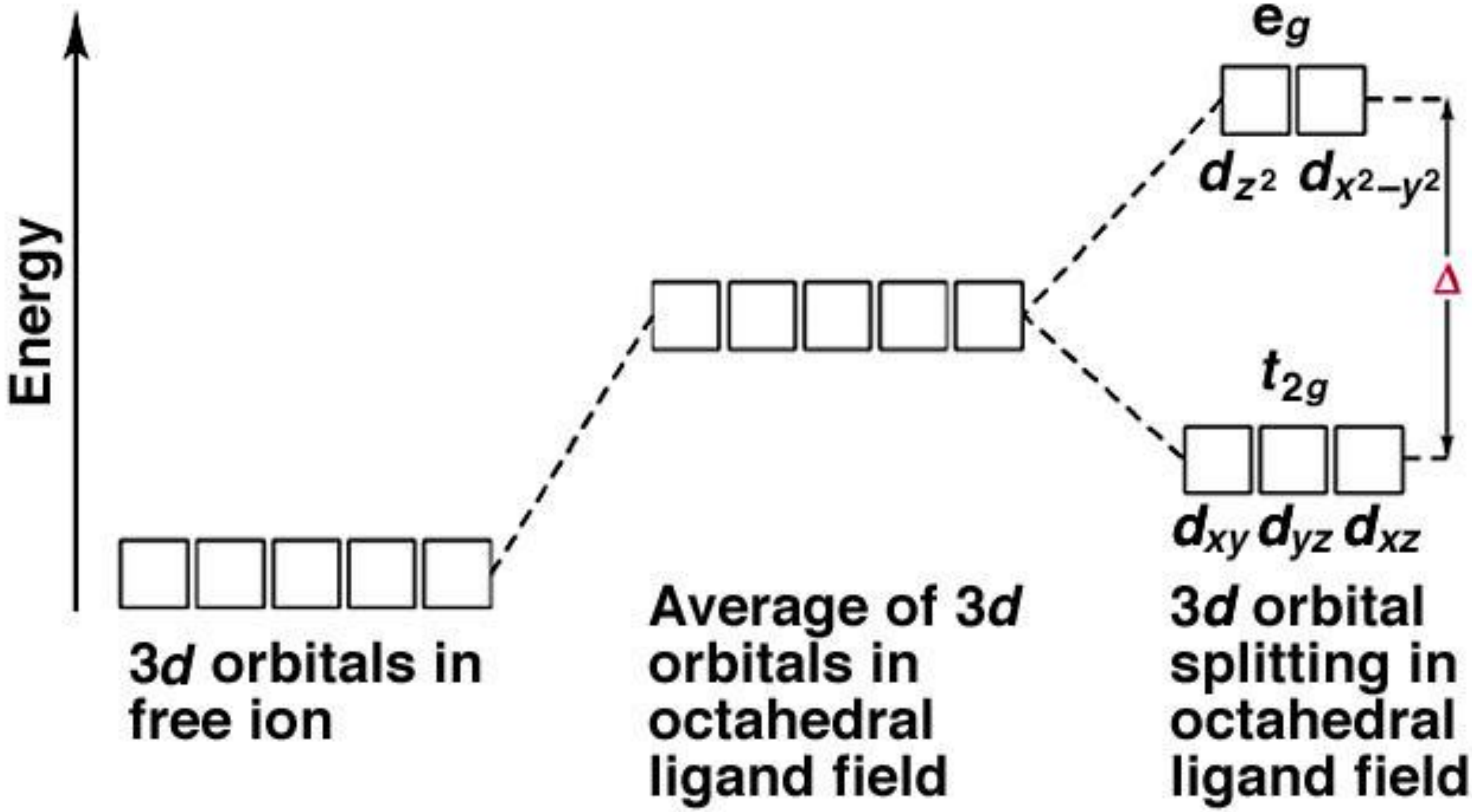
strong-field (low-spin): large splitting of *d* orbitals

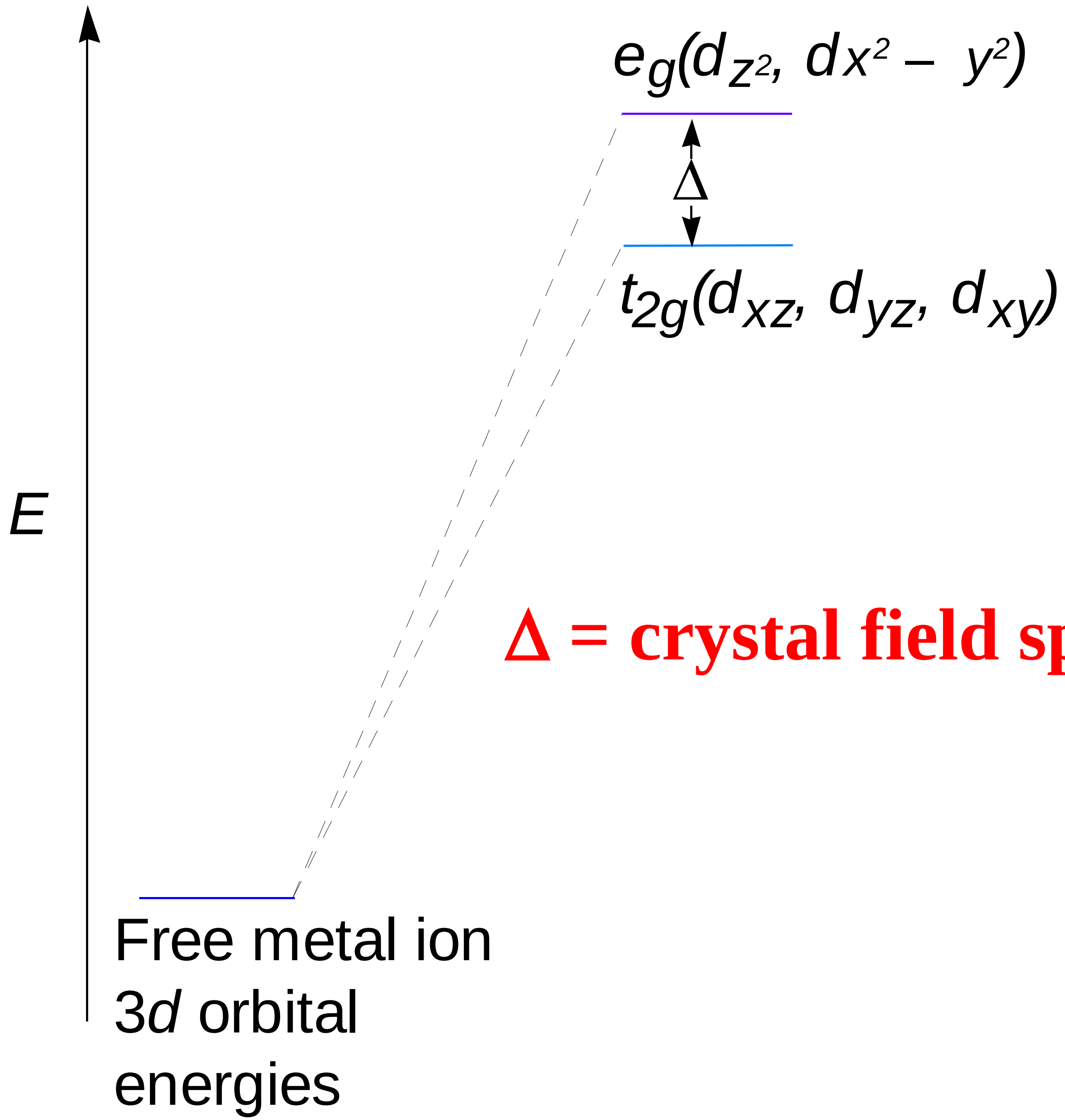
weak-field (high-spin): small splitting of *d* orbitals

d Orbitals in an Octahedral Field of Ligands



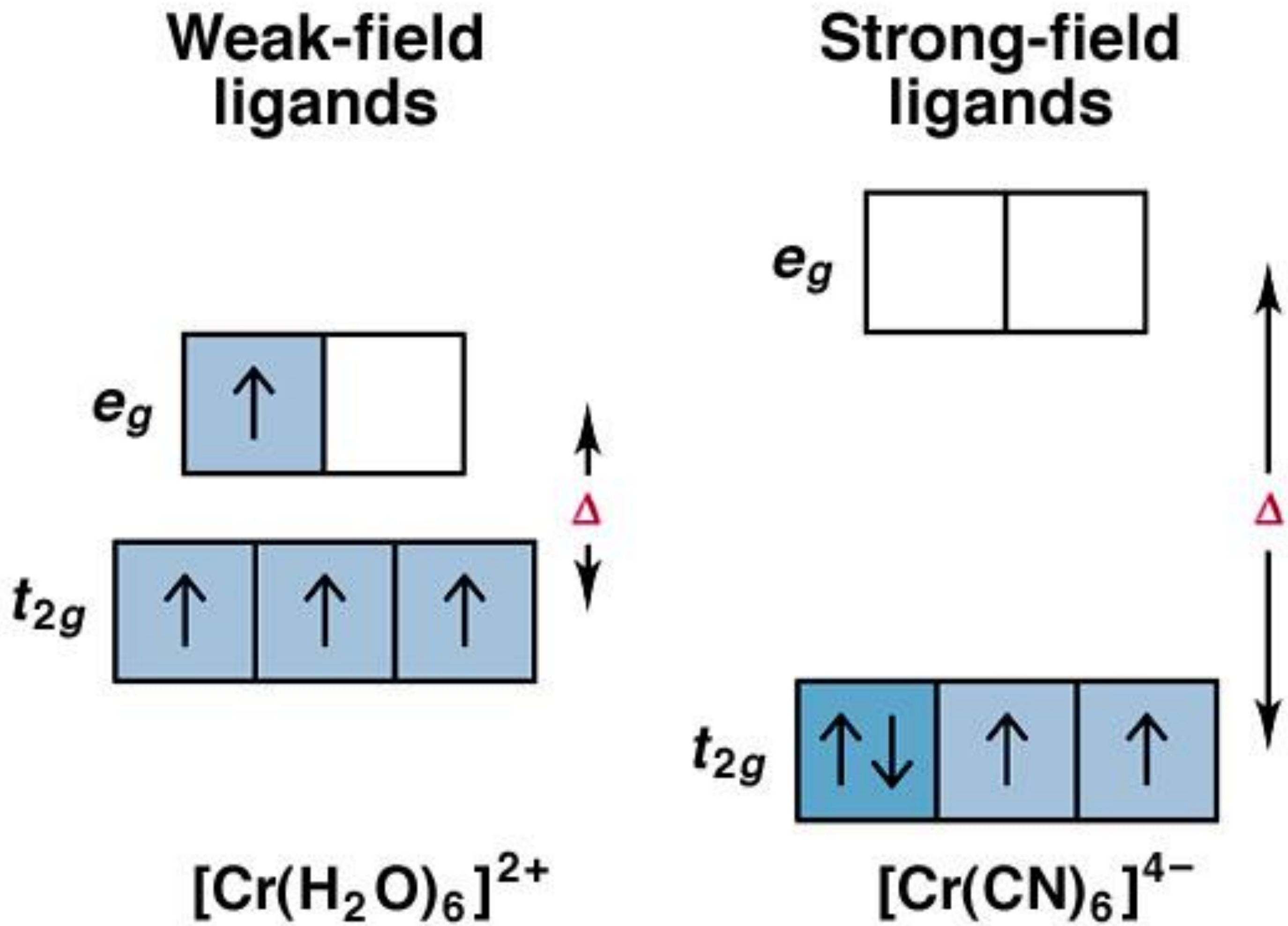
Splitting of *d*-Orbital Energies by an Octahedral Field of Ligands





Δ = crystal field splitting

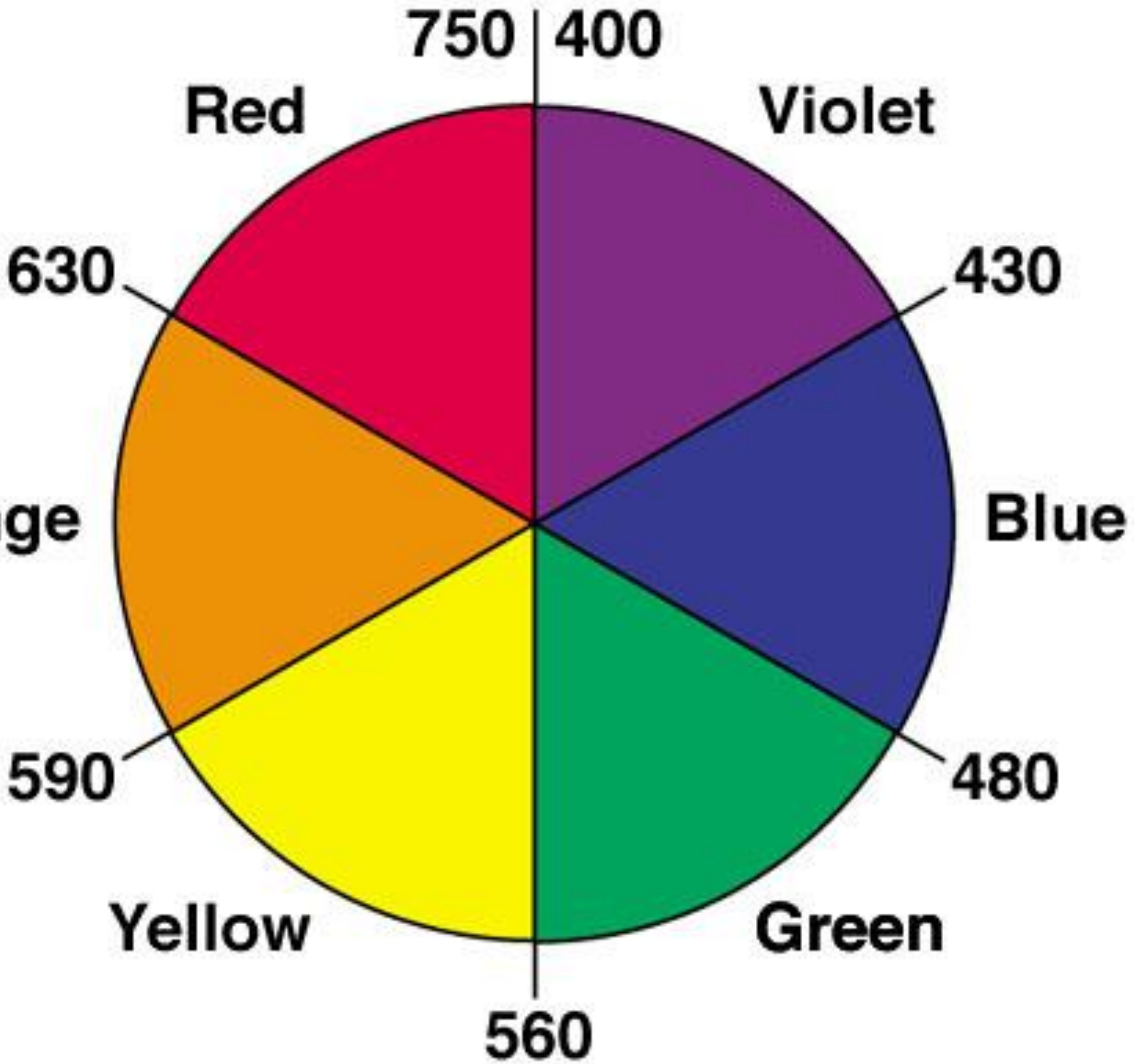
Effect of the Ligand on Splitting Energy



High spin

Low spin

An Artist's Wheel

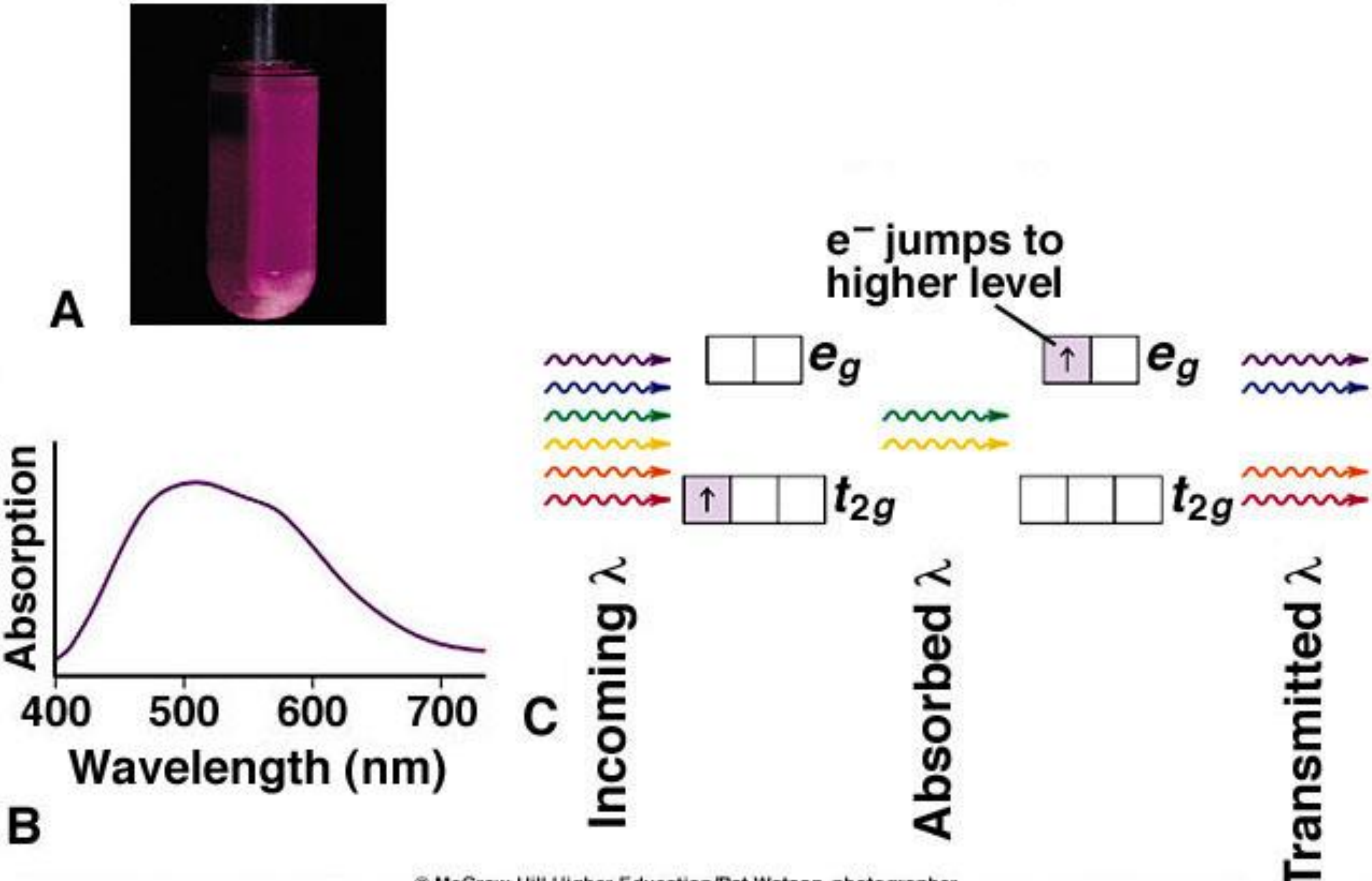


Absorbed and Observed Color

Table 23.11 Relation Between Absorbed and Observed Colors

Absorbed Color	λ(nm)	Observed Color	λ(nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

The Color of $[Ti(H_2O)_6]^{3+}$



Effects of Metal Oxidation State and of Ligand on Color

A

B

The Spectrochemical Series

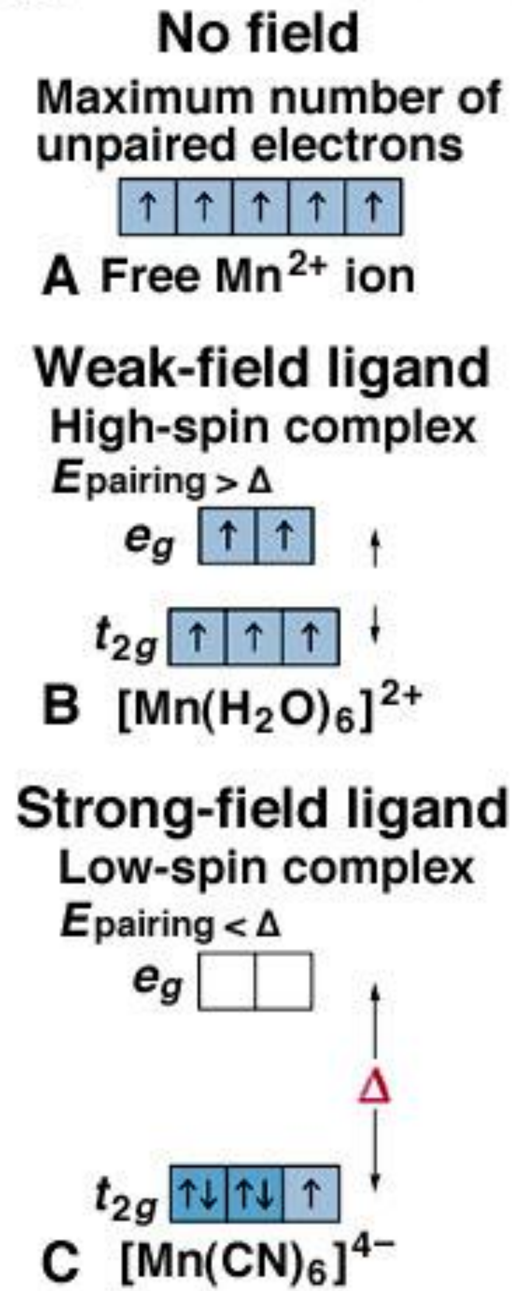
$I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < en < NO_2^- < CN^- < CO$

WEAKER FIELD → STRONGER FIELD

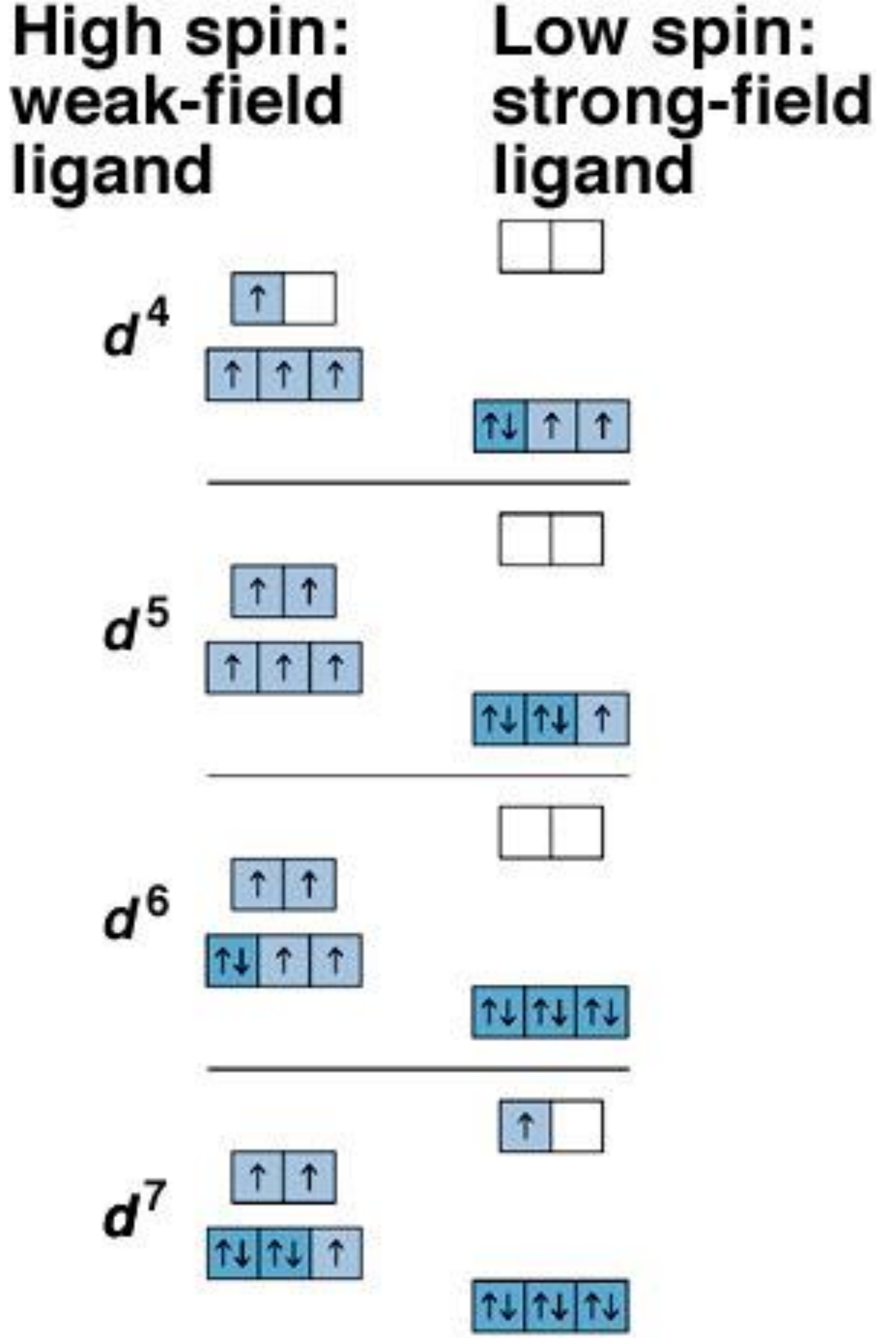
SMALLER Δ → LARGER Δ

LONGER λ → SHORTER λ

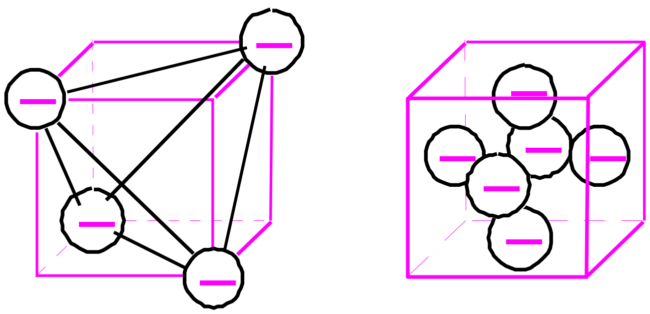
High-Spin and Low-Spin Complex Ions of Mn^{2+}

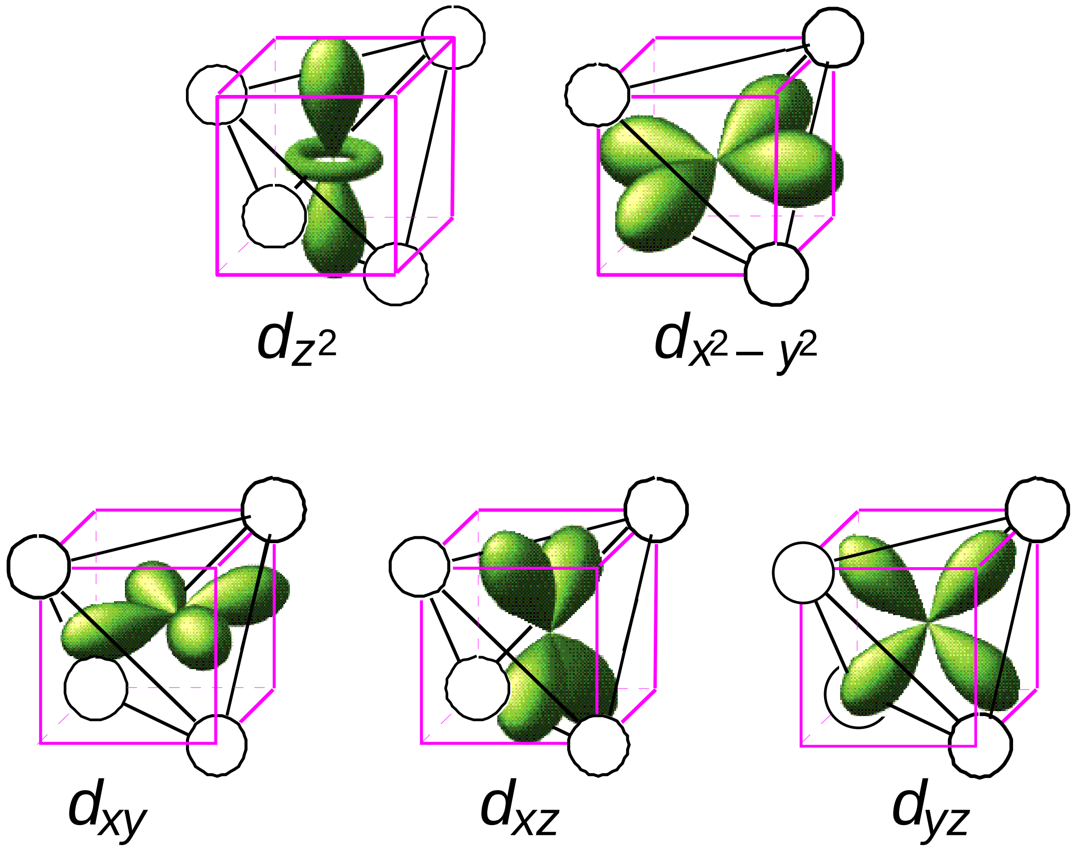


Orbital Occupancy for High- and Low-Spin Complexes of d^4 through d^7 Metal Ions.

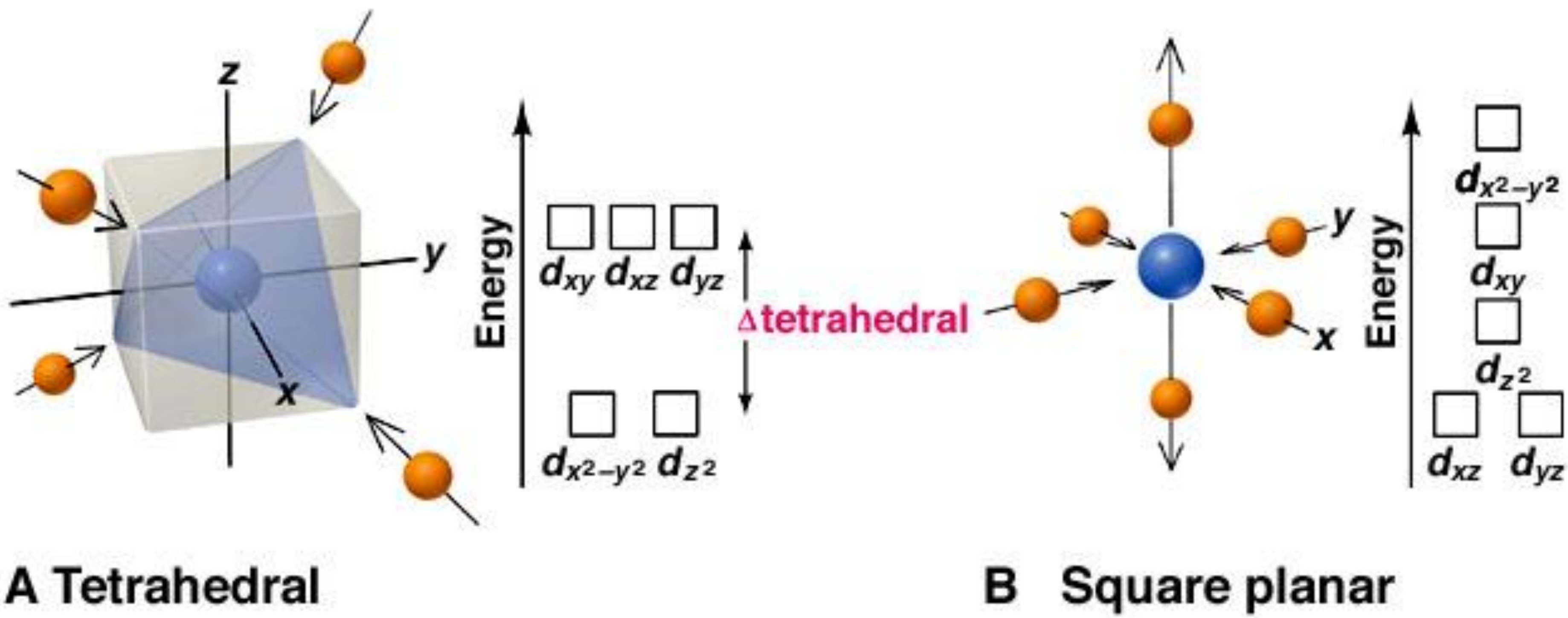


Tetrahedral Complexes

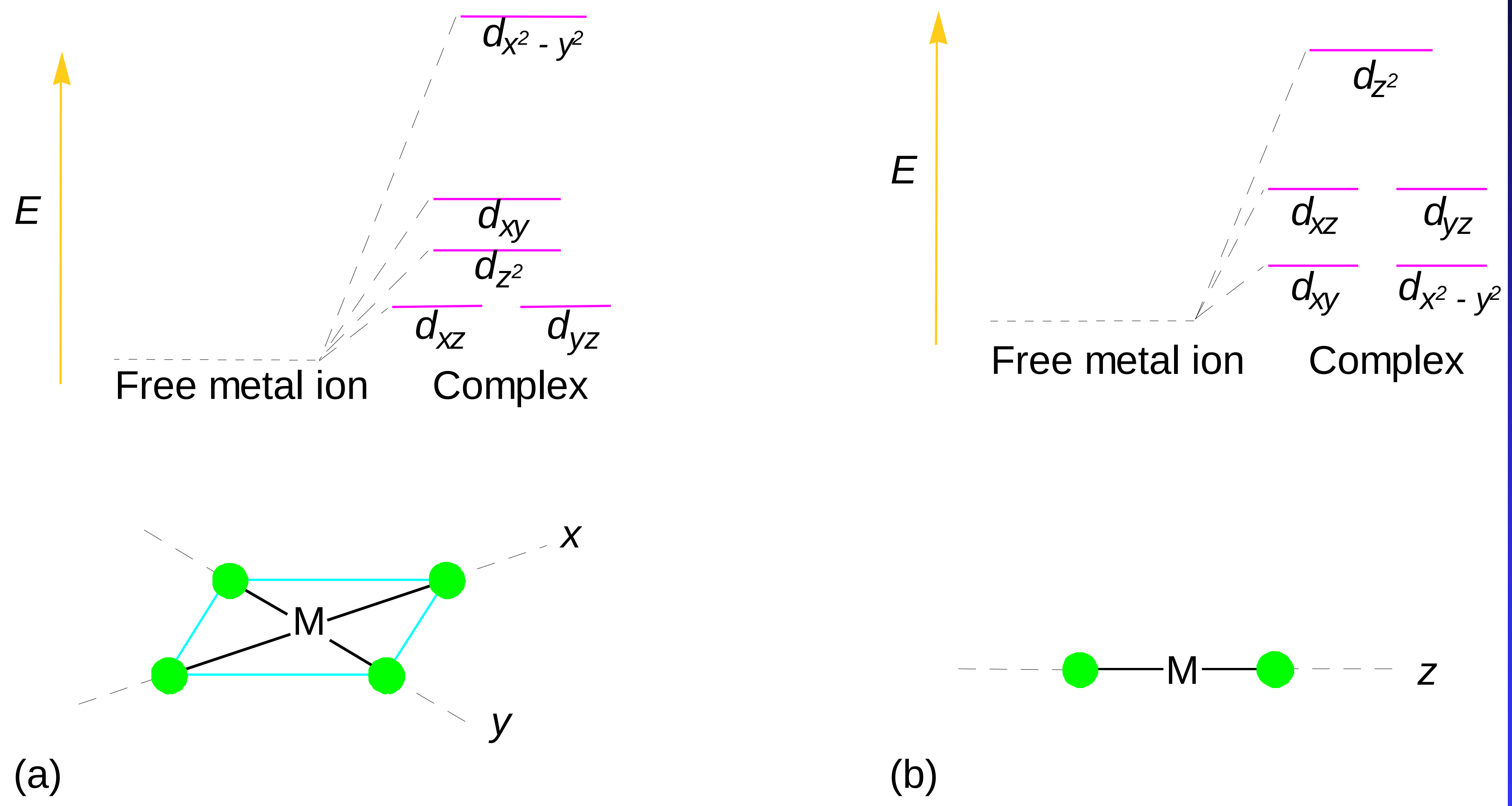




Splitting of *d*-Orbitals Energies



Square Planar & Linear Complexes



Approach along x-and y-axes

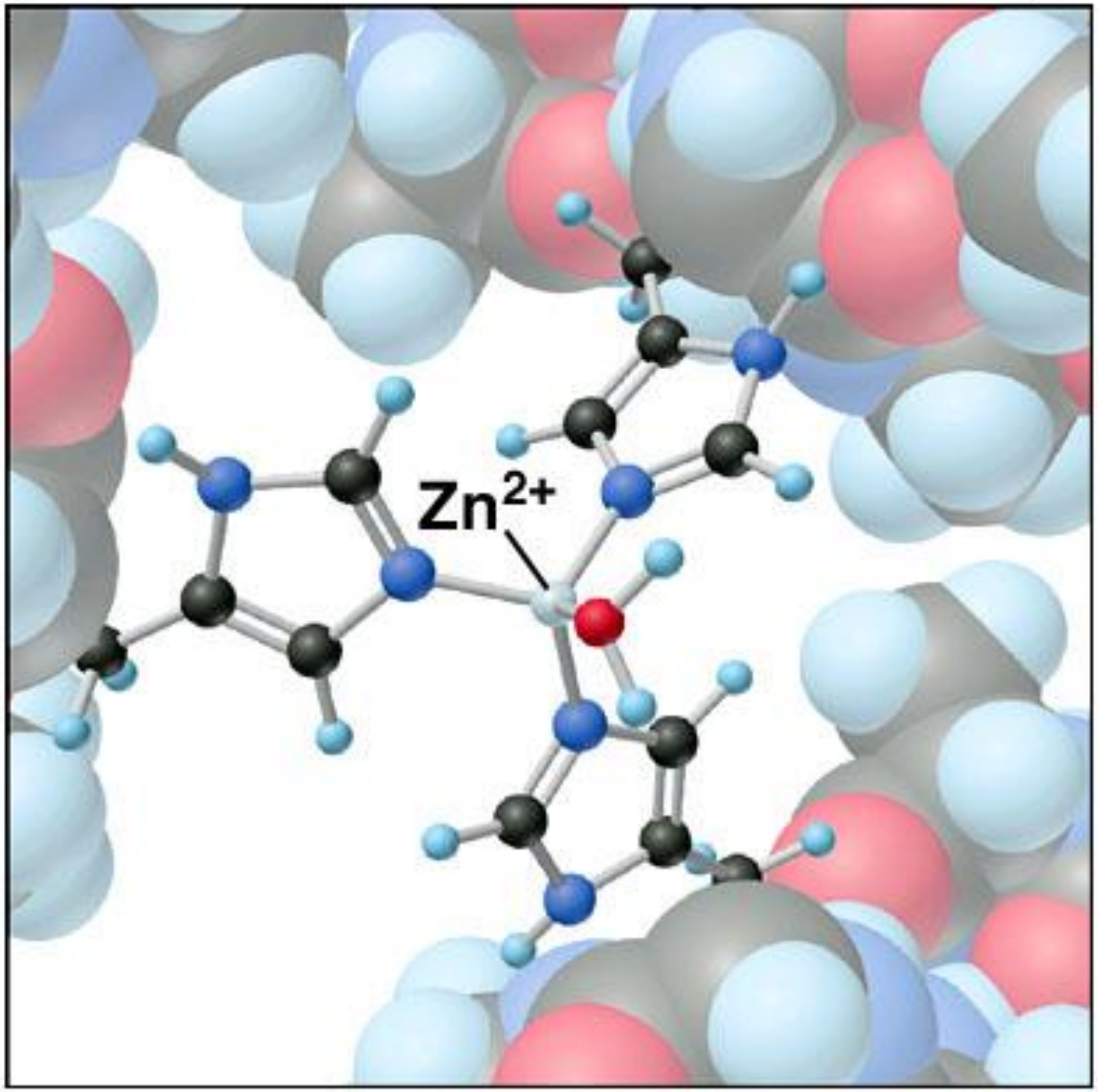
Approach along z-axis

Transiton Metal Trace Elements in Humans

Table 23.A Some Transition Metal Trace Elements in Humans

Element	Biomolecule Containing Element	Function of Biomolecule
Vanadium	Protein (?)	Redox couple in fat metabolism (?)
Chromium	Glucose tolerance factor	Glucose utilization
Manganese	Isocitrate dehydrogenase	Cell respiration
Iron	Hemoglobin and myoglobin Cytochrome *c* Catalase	Oxygen transport Cell respiration; ATP formation Decomposition of H_2O_2
Cobalt	Cobalamin (vitamin B_{12})	Development of red blood cells
Copper	Ceruloplasmin Cytochrome oxidase	Hemoglobin synthesis Cell respiration; ATP formation
Zinc	Carbonic anhydrase Carboxypeptidase A Alcohol dehydrogenase	Elimination of CO_2 Protein digestion Metabolism of ethanol

Tetrahedral Zn^{2+} Complex in Carbonic Anhydrase



Hemoglobin & Oxyhemoglobin