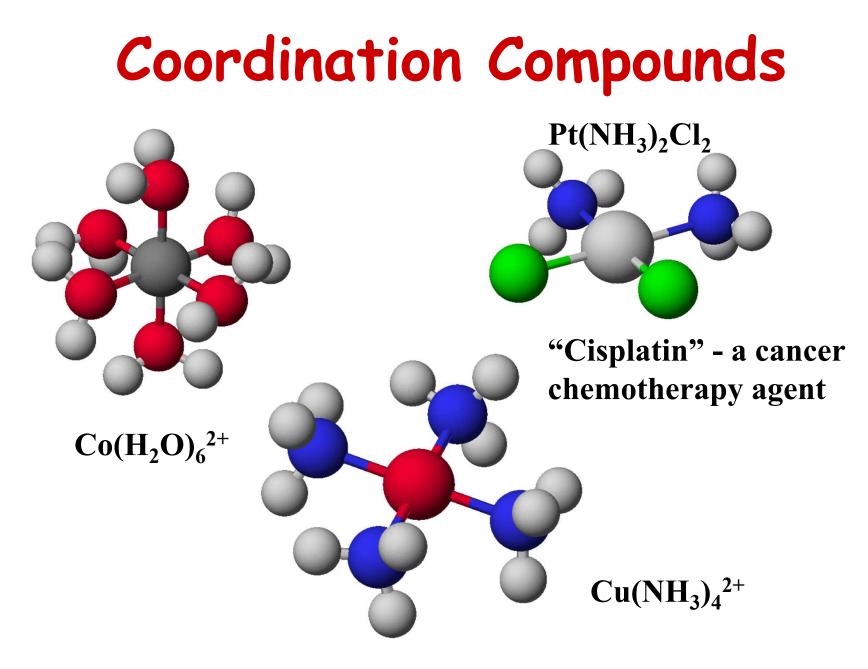


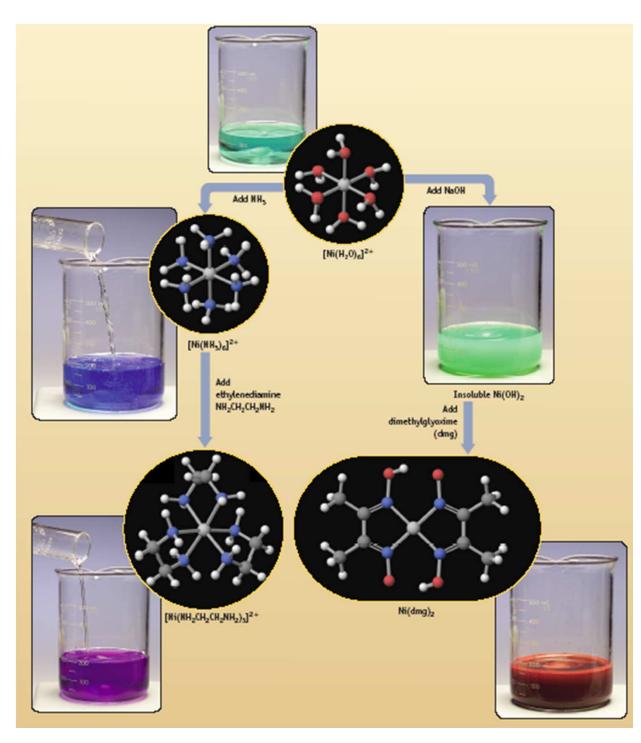


Electron Configurations

Main groups									Main groups									
(s-block elements)								(p-block elements)										
	1 1A																	18 8A
	1 H	2 2A			Tra	ansit	ion n	netal	grou	ups			13 3A	14 4A	15 5A	16 6A	17 7A	2 He
	3 4 Li Be				_				ents	-			5 B	6 0	7 N	8 0	9 F	10 Ne
	11 Na	12 Mg	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 - 8B -	10 	11 1B	12 2B	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 	54 Xe
	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 TI	82 Pb	83 Bi	84 Po	85 At	86 Rn
	86 Fr	88 Ra	89 Ac	104 Rf		106 Sg		108 Hs	1.1.1.1	110 Ds	111 Rg	112		114		116		
Inner transition Lant	hani	des	58	59 Pr	60 Nd	61 Bm	62 Sm	63 E	64 6d	65 Th	66 Dv	67	68 Er	69 Tm	70 Yb	71		
elements (f-block elements) A	ctini	des	Ce 90 Th	91	Nd 92	Pm 93 Np	Sm 94	Eu 95	Gd 96	Tb 97	Dy 98	Ho 99 50	Er 100	Tm 101	102	Lu 103		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

Figure 20-1 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.





Coordination Compounds of Ni²⁺

Electron Configurations

Zn (<i>Z</i> = 30): [Ar] 3 <i>d</i> ¹⁰ 4 <i>s</i> ²						
Cu (<i>Z</i> = 29)						
$\frac{\uparrow\downarrow}{4s^2} \qquad \frac{\uparrow\downarrow}{3d^9} \stackrel{\uparrow\downarrow}{\longrightarrow} \stackrel{\uparrow\downarrow}{4s^2} \qquad \frac{\uparrow\downarrow}{4s^2}$						
$\frac{\uparrow}{4s^1} \qquad \frac{\uparrow\downarrow}{3d^{10}} \stackrel{\uparrow\downarrow}{=} \frac{\uparrow\downarrow}{4s^1} \stackrel{\uparrow\downarrow}{=} \frac{\uparrow}{4s^1}$						
$\frac{\uparrow}{3d^6} \stackrel{\uparrow}{\longrightarrow} \frac{\uparrow}{f} Fe^{3+} \stackrel{\uparrow}{\longrightarrow} \frac{\uparrow}{3d^5} \stackrel{\uparrow}{\longrightarrow} \frac{\uparrow}{f}$						

Unnumbered 20 p815b Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

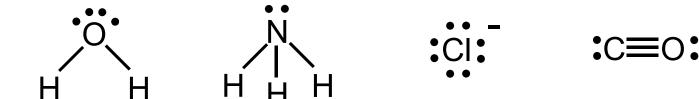
Omit 20.2 - 20.4 Coordination Compounds

Many *coordination compound* consists of a complex ion.

A *complex ion* contains a central metal cation bonded to one or more molecules or ions.

The molecules or ions that surround the metal in a complex ion are called *ligands*.

A ligand has **at least one** unshared pair of valence electrons



 NH_3

NH₃

NH₂

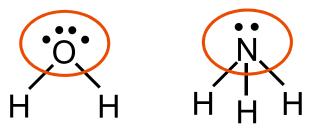
C

Cl

Coordination Compounds

The atom in a ligand that is bound directly to the metal atom is

the **donor** atom.



Ligands with:

one donor atom	monodentate	H₂O, NH₃, CI⁻
two donor atoms	bidentate	ethylenediamine
three or more donor atoms	polydentate	EDTA

The number of donor atoms surrounding the central metal atom in a complex ion is the *coordination number*.

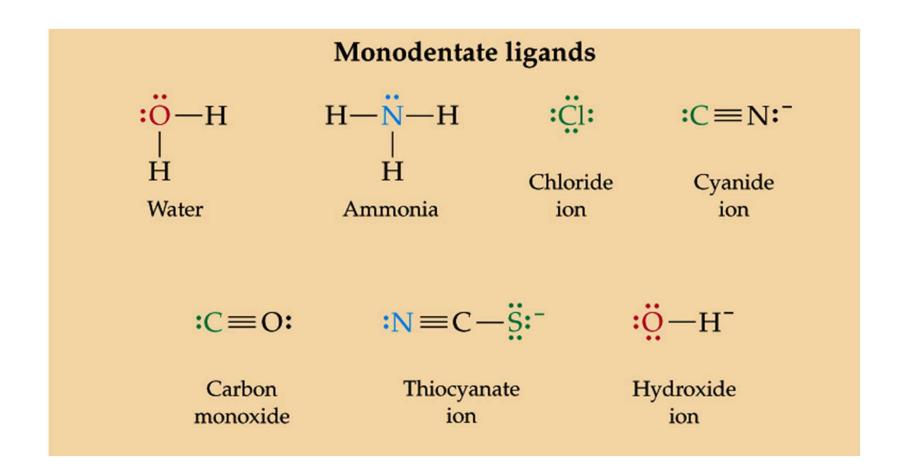
Coordination Compounds

Coordination Number: The number of ligand donor atoms that surround a central metal ion or atom.

TABLE 20.4 Examples of Complexes with Various Coordination Numbers

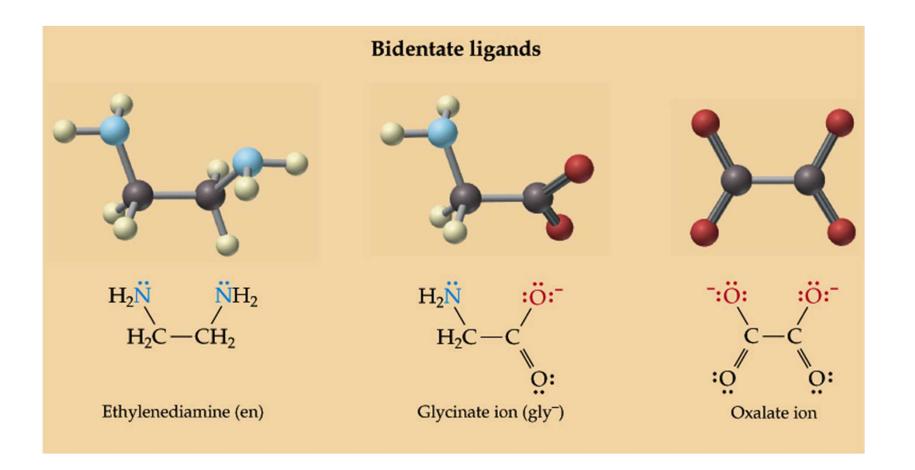
Coordination Number	Complex
2	[Ag(NH ₃) ₂]⁺, [CuCl ₂] [−]
3	[Hgl ₃] [_]
4	[Zn(NH ₃) ₄] ²⁺ , [Ni(CN) ₄] ^{2–}
5	[Ni(CN) ₅] ^{3–} , Fe(CO) ₅
6	[Cr(H ₂ O) ₆] ³⁺ , [Fe(CN) ₆] ³⁻
7	[ZrF ₇] ^{3–}
8	[Mo(CN) ₈] ^{4–}

Ligands



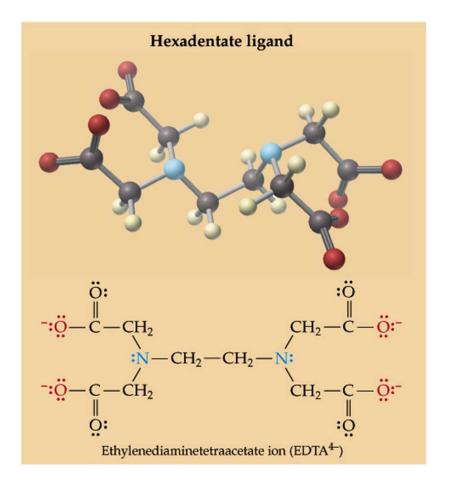
Ligands

03

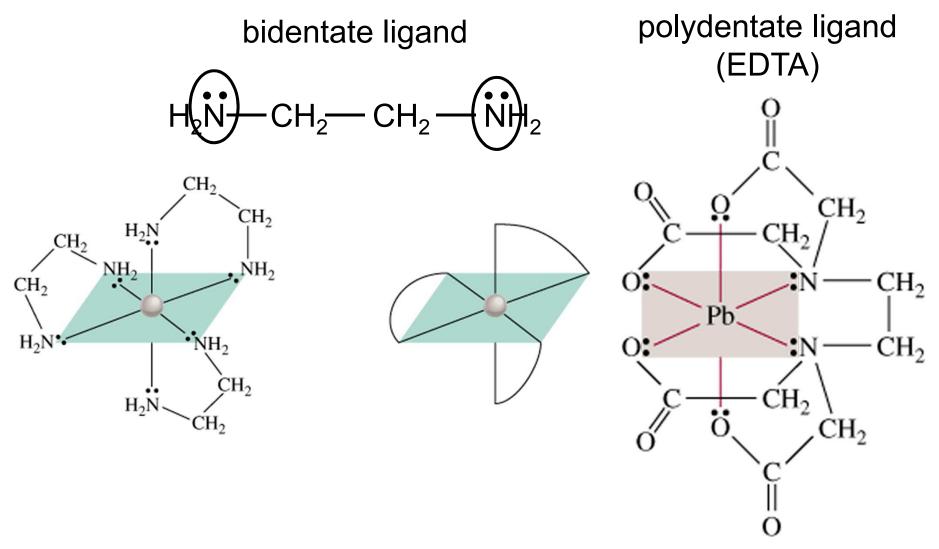


Poly DentateLigands

- EDTA⁴⁻ is often used to treat heavy metal poisoning such as Hg²⁺, Pb²⁺, and Cd²⁺.
- EDTA⁴⁻ bonds to Pb²⁺, which is excreted by the kidneys as [Pb(EDTA)]²⁻.



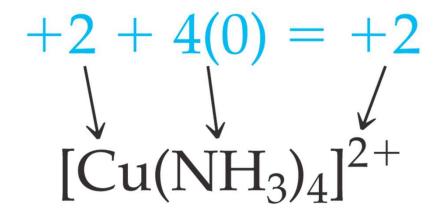
Coordination Compounds



Bidentate and polydentate ligands are called *chelating agents*

Chapter 20

What is the Oxidation Numbers of Cu?



Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.

What is the charge on the following Complex, If the Oxidation number of Cr is +3?

$$+3 + 4(0) + 2(-1) = +1$$

 $\downarrow \qquad /$
 $Cr(H_2O)_4Cl_2$

Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

What are the oxidation numbers of the metals in $K[Au(OH)_4]$ and $[Cr(NH_3)_6](NO_3)_3$?

OH⁻ has charge of -1

K⁺ has charge of +1

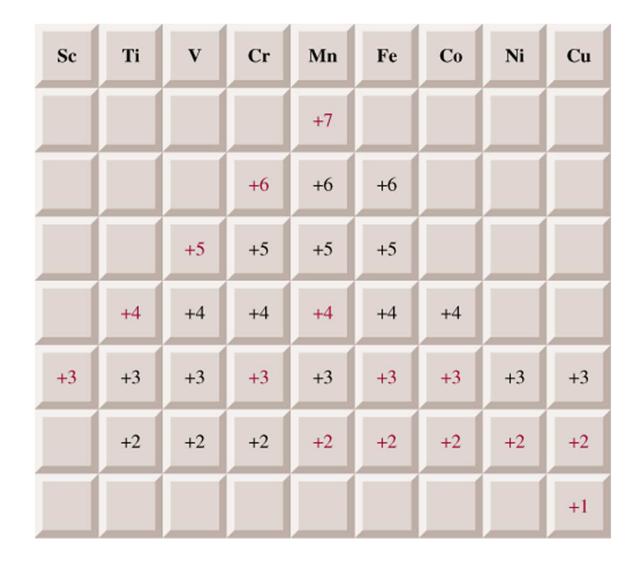
? Au + 1 + 4x(-1) = 0

Au = +3

 NO_3^- has charge of -1 NH₃ has no charge ? Cr + 6x(0) + 3x(-1) = 0 Cr = +3

Oxidation States of the 1st Row Transition Metals

(most stable oxidation numbers are shown in red)

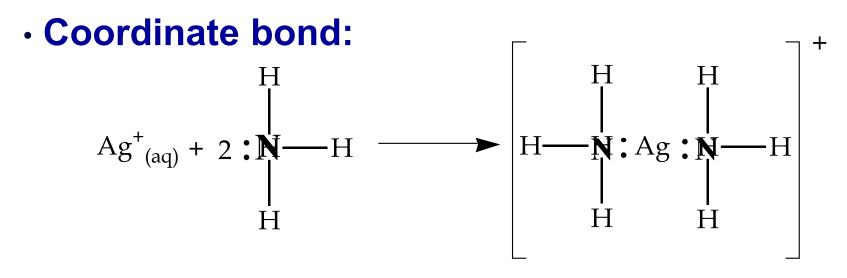


Learning Check

A complex ion contains a Cr^{3+} bound to four H_2O molecules and two CI^- ions. Write its formula.

+1 $[Cr(H_2O)_4Cl_2]$

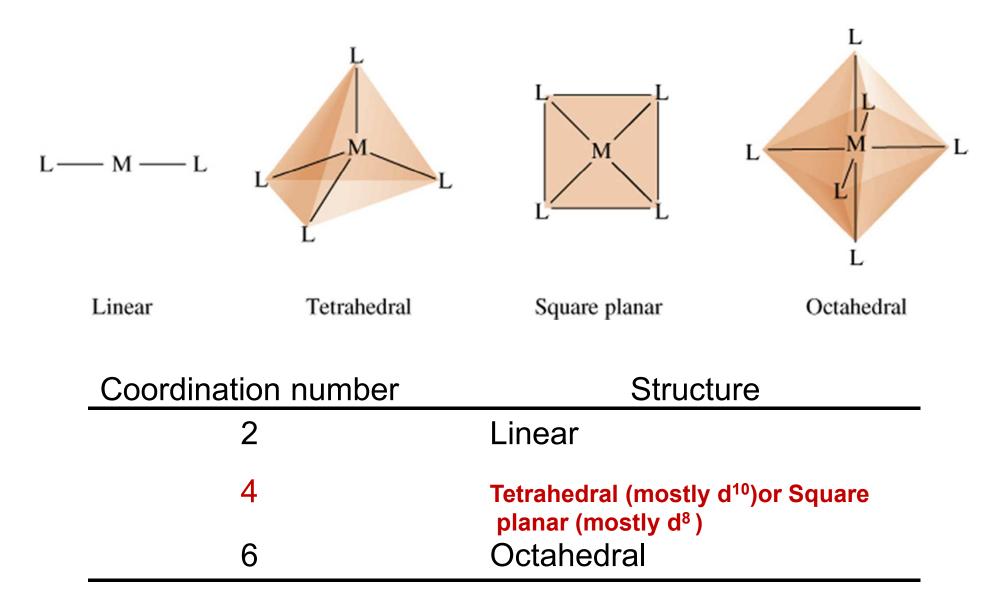
Writing Formula for Coordinated Complex



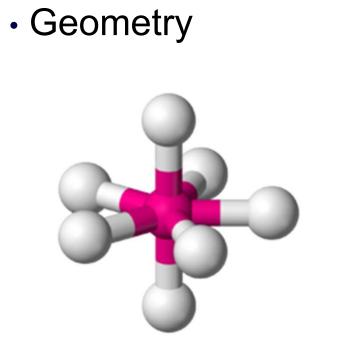
• Coordination Sphere: is the central metal and surrounding ligands. The square brackets separate the complex from counter ions such as SO_4^{2-} .

 $[Ag(NH_3)_2]_2 SO_4$

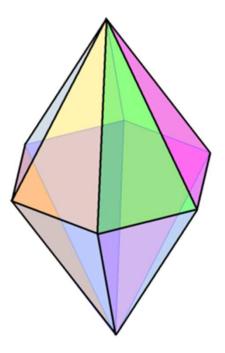
Geometry of Coordination Compounds



Coordination Number of 7&8

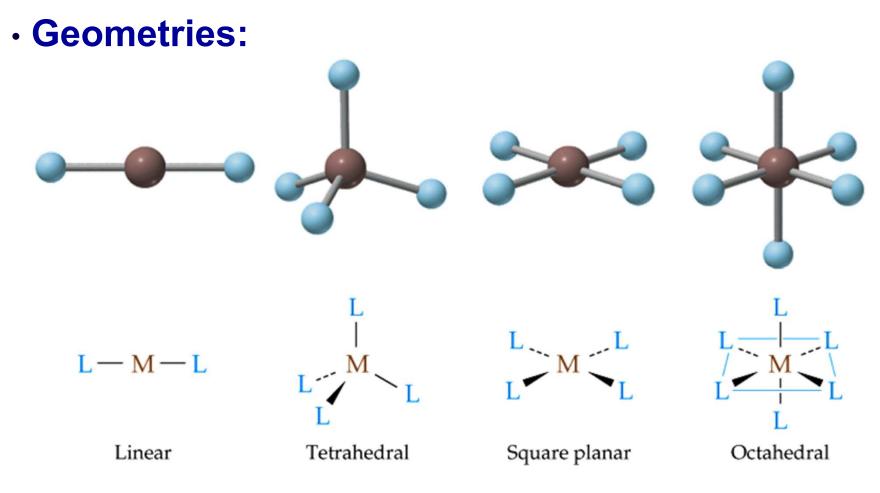


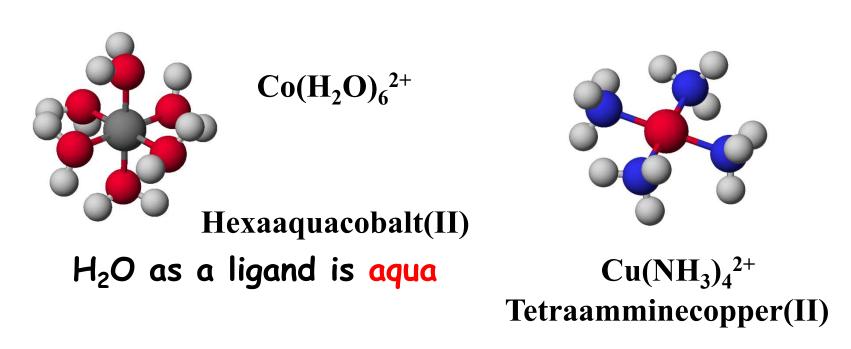
Pentagonal bipyramid



Hexagonal bipyramid

Coordination Compounds





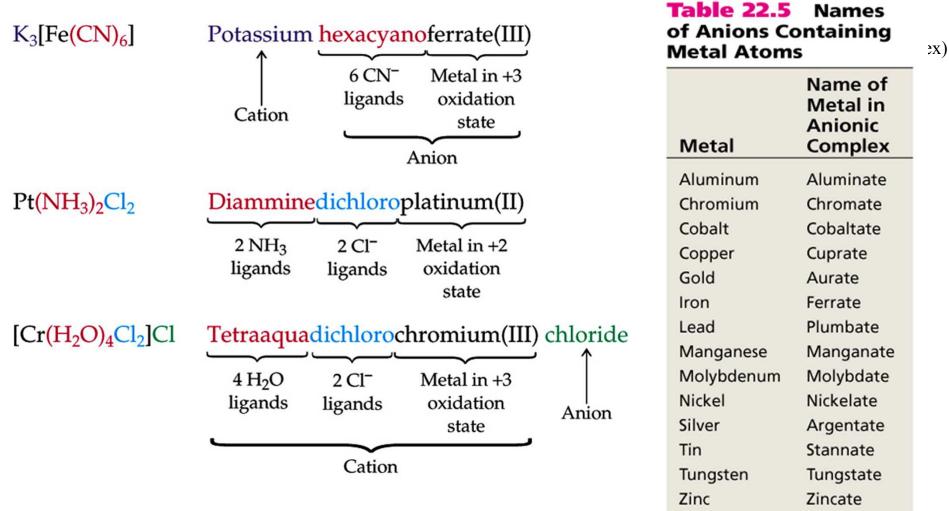


Systematic naming specifies the type and number of ligands, the metal, and its oxidation state.

Ligand's Names

TABLE 20.5 Names of Some Common Ligands						
Anionic Ligand	Ligand Name	Neutral Ligand	Ligand Name			
Bromide, Br ⁻ Carbonate, CO_3^{2-} Chloride, Cl ⁻ Cyanide, CN ⁻ Fluoride, F ⁻ Glycinate, gly ⁻ Hydroxide, OH ⁻ Oxalate, $C_2O_4^{2-}$ Thiocyanate, SCN ⁻	Bromo Carbonato Chloro Cyano Fluoro Glycinato Hydroxo Oxalato Thiocyanato [*] Isothiocyanato [†]	Ammonia, NH ₃ Water, H ₂ O Carbon monoxide, CO Ethylenediamine, en	Ammine Aqua Carbonyl Ethylenediamine			

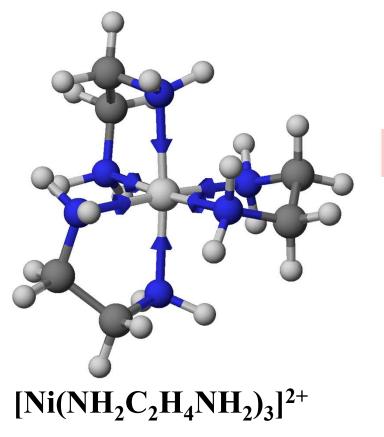
* Ligand donor atom is S. ⁺Ligand donor atom is N.



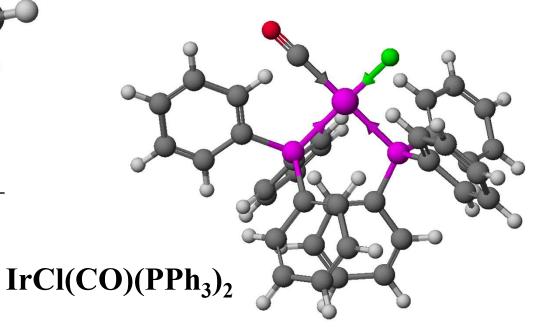
Systematic naming follows IUPAC rules:

- If compound is a salt, name cation first and then the anion, just as in naming simple salts.
- In naming a complex ion or neutral complex, name ligands first and then the metal.
- If the complex contains more than one ligand of a particular type, indicate the number with the appropriate Greek prefix: *di*–, *tri*–, *tetra*–, *penta*–, *hexa*–.

- If the name of a ligand itself contains a Greek prefix,
 (ethylenediamine or triphenylphosphine) put the ligand name in parentheses and use: bis (2), tris (3), or tetrakis (4).
- Use a Roman numeral in parentheses, immediately following the name of the metal, to indicate the metal's oxidation state.
- In naming the metal, use the ending <u>–ate</u> if metal is in an anionic complex.



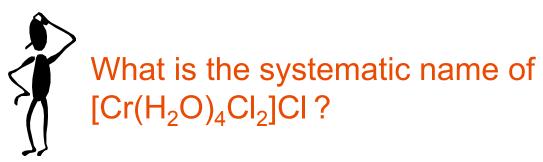
Tris(ethylenediamine)nickel(II)



Carbonylchlorobis(triphenylphosphine)iridium(I)

Table 22.5 Names of Anions Containing Metal Atoms

Metal	Name of Metal in Anionic Complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

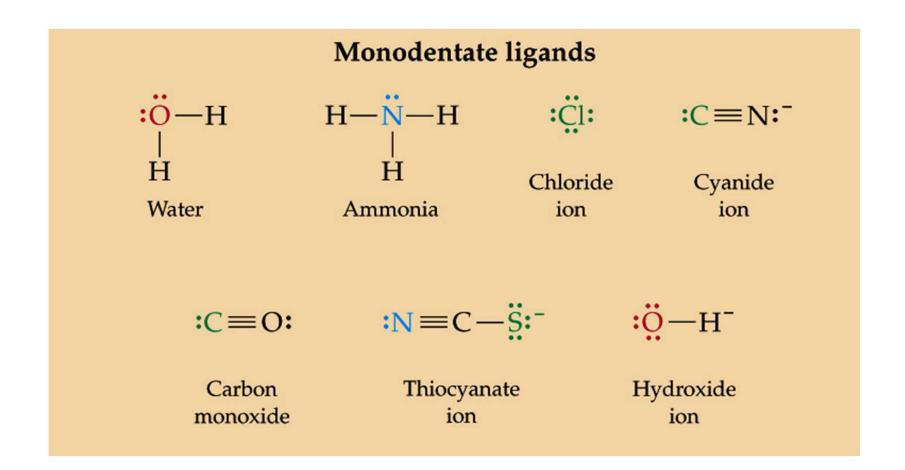


tetraaquadichlorochromium(III) chloride

Write the formula of tris(ethylenediamine)cobalt(II) sulfate

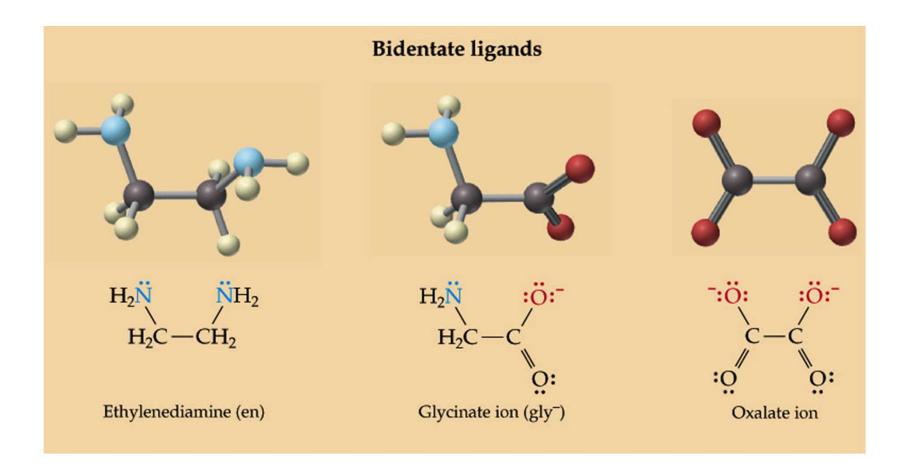
 $[Co(en)_3]SO_4$

Ligands



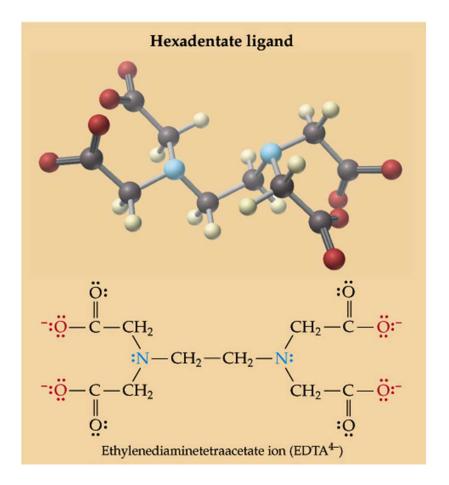
Ligands

03

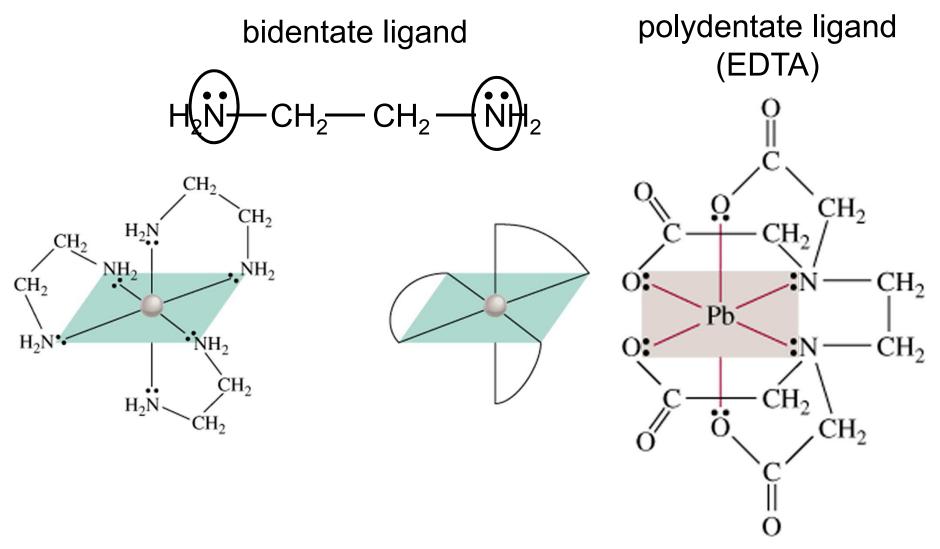


Poly DentateLigands

- EDTA⁴⁻ is often used to treat heavy metal poisoning such as Hg²⁺, Pb²⁺, and Cd²⁺.
- EDTA⁴⁻ bonds to Pb²⁺, which is excreted by the kidneys as [Pb(EDTA)]²⁻.



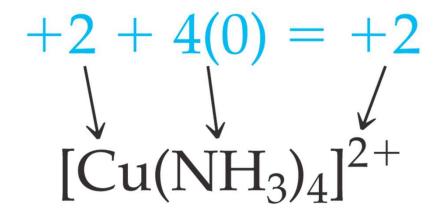
Coordination Compounds



Bidentate and polydentate ligands are called *chelating agents*

Chapter 20

What is the Oxidation Numbers of Cu?



Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.

Oxidation Number Rules

Rule	Applies to	Statement
1	Elements	The oxidation number of an atom in an element is zero.
2	Monatomic ions	The oxidation number of an atom in a monatomic ion equals the charge of the ion.
3	Oxygen	The oxidation number of oxygen is -2 in most of its compounds. (An exception is O in H_2O_2 and other peroxides, where the oxidation number is -1 .)

Oxidation Number Rules

Rule	Applies to	Statement
4	Hydrogen	+1, it will be -1 when hydrogen comes with metal. NaH
5	Halogens	Fluorine is –1 in all its compounds. Each of the other halogens is –1 in binary compounds unless the other element is oxygen.
6	Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum in a polyatomic ion equals the charge on the ion.

What is the charge on the following Complex, If the Oxidation number of Cr is +3?

$$+3 + 4(0) + 2(-1) = +1$$

 $\downarrow \qquad /$
 $Cr(H_2O)_4Cl_2$

Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

What are the oxidation numbers of the metals in $K[Au(OH)_4]$ and $[Cr(NH_3)_6](NO_3)_3$?

OH⁻ has charge of -1

K⁺ has charge of +1

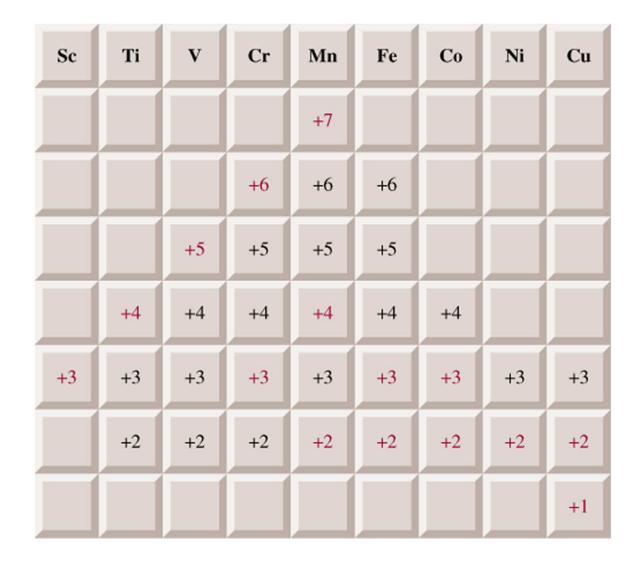
? Au + 1 + 4x(-1) = 0

Au = +3

 NO_3^- has charge of -1 NH₃ has no charge ? Cr + 6x(0) + 3x(-1) = 0 Cr = +3

Oxidation States of the 1st Row Transition Metals

(most stable oxidation numbers are shown in red)

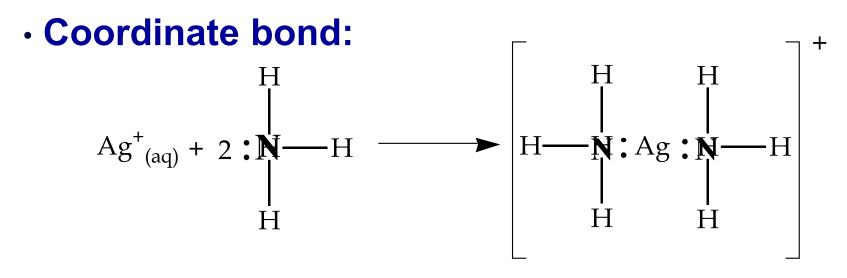


Learning Check

A complex ion contains a Cr^{3+} bound to four H_2O molecules and two CI^- ions. Write its formula.

+1 $[Cr(H_2O)_4Cl_2]$

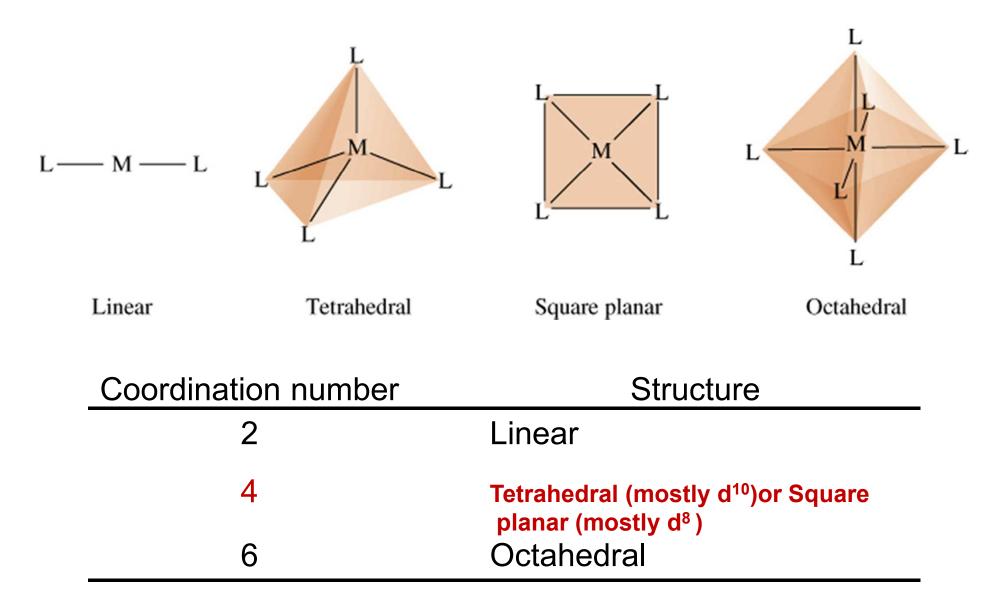
Writing Formula for Coordinated Complex



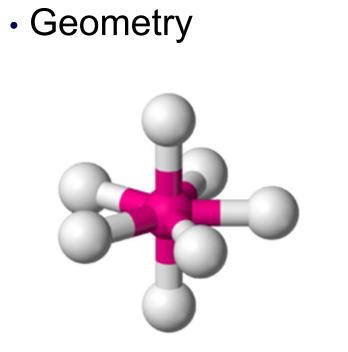
• Coordination Sphere: is the central metal and surrounding ligands. The square brackets separate the complex from counter ions such as SO_4^{2-} .

 $[Ag(NH_3)_2]_2 SO_4$

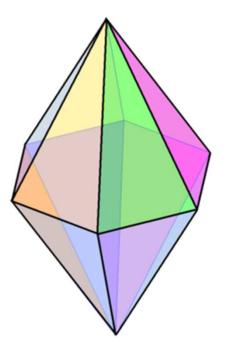
Geometry of Coordination Compounds



Coordination Number of 7&8

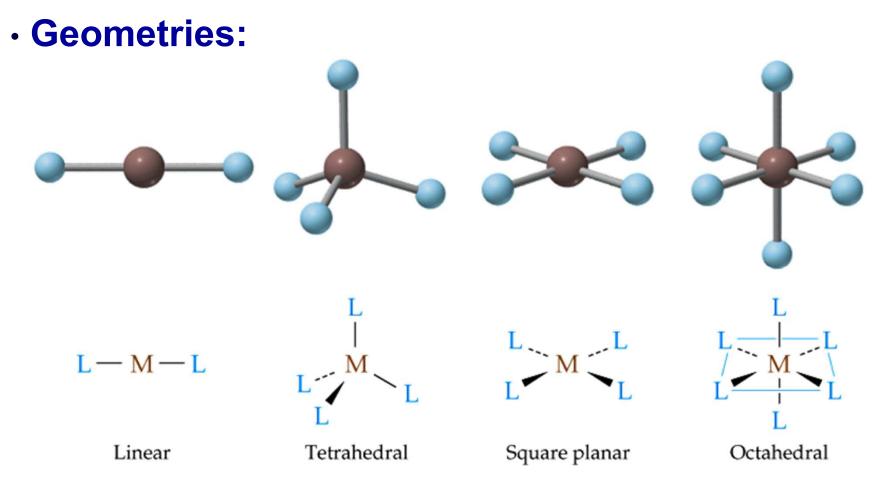


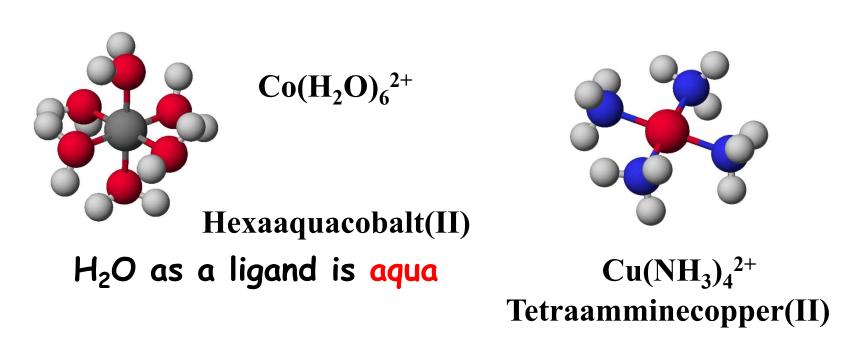
Pentagonal bipyramid



Hexagonal bipyramid

Coordination Compounds







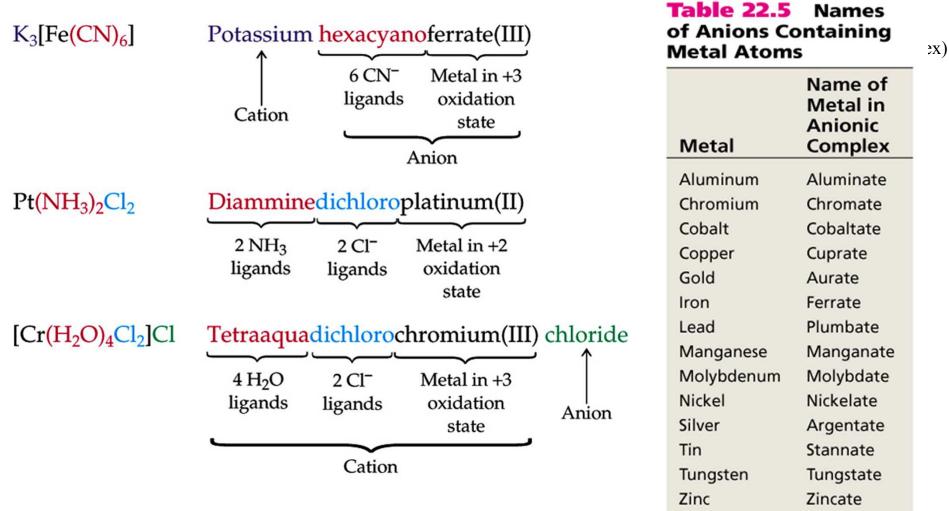
Systematic naming specifies the type and number of ligands, the metal, and its oxidation state.

Ligand's Names

TABLE 20.5 Names of Some Common Ligands

Anionic Ligand	Ligand Name	Neutral Ligand	Ligand Name
Bromide, Br ⁻ Carbonate, CO_3^{2-} Chloride, Cl ⁻ Cyanide, CN ⁻ Fluoride, F ⁻ Glycinate, gly ⁻ Hydroxide, OH ⁻ Oxalate, $C_2O_4^{2-}$ Thiocyanate, SCN ⁻	Bromo Carbonato Chloro Cyano Fluoro Glycinato Hydroxo Oxalato Thiocyanato [*] Isothiocyanato [†]	Ammonia, NH ₃ Water, H ₂ O Carbon monoxide, CO Ethylenediamine, en	Ammine Aqua Carbonyl Ethylenediamine

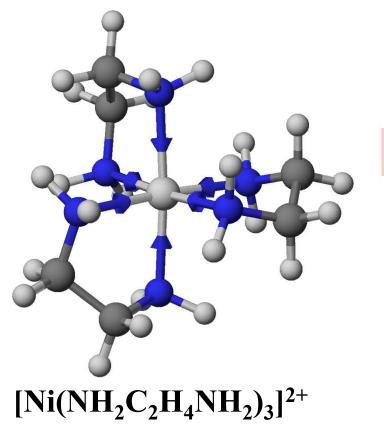
* Ligand donor atom is S. ⁺Ligand donor atom is N.



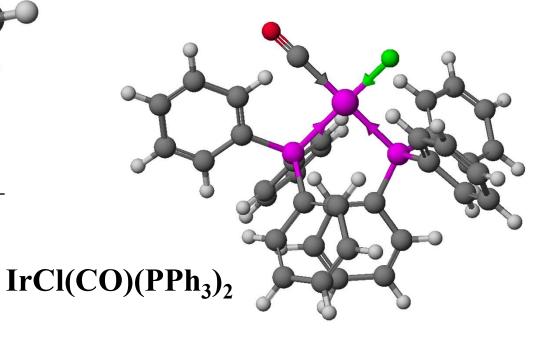
Systematic naming follows IUPAC rules:

- If compound is a salt, name cation first and then the anion, just as in naming simple salts.
- In naming a complex ion or neutral complex, name ligands first and then the metal.
- If the complex contains more than one ligand of a particular type, indicate the number with the appropriate Greek prefix: *di*-, *tri*-, *tetra*-, *penta*-, *hexa*-.

- If the name of a ligand itself contains a Greek prefix,
 (ethylenediamine or triphenylphosphine) put the ligand name in parentheses and use: bis (2), tris (3), or tetrakis (4).
- Use a Roman numeral in parentheses, immediately following the name of the metal, to indicate the metal's oxidation state.
- In naming the metal, use the ending <u>–ate</u> if metal is in an anionic complex.



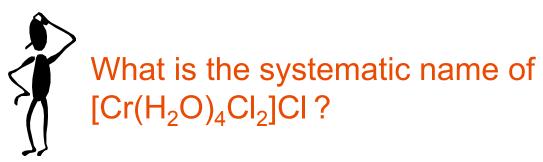
Tris(ethylenediamine)nickel(II)



Carbonylchlorobis(triphenylphosphine)iridium(I)

Table 22.5 Names of Anions Containing Metal Atoms

Metal	Name of Metal in Anionic Complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate



tetraaquadichlorochromium(III) chloride

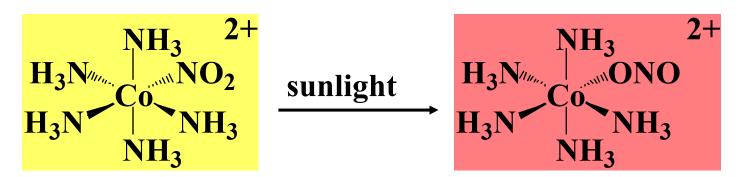
Write the formula of tris(ethylenediamine)cobalt(II) sulfate

 $[Co(en)_3]SO_4$

Constitutional Isomerism

- **1. Constitutional Isomers:** Have different connections among their constituent atoms.
 - Ionization Isomers :
 - $[Co(NH_3)_5Br]SO_4$ (violet compound with Co–Br bond), $[Co(NH_3)_5SO_4]Br$ (red compound with Co–SO₄ bond).
 - Linkage Isomers form when a ligand can bond through two different donor atoms. Consider $[Co(NH_3)_5NO_2]^{2+}$ which is yellow with the Co–NO₂ bond and red with the Co–ONO bond.

Linkage Isomerism

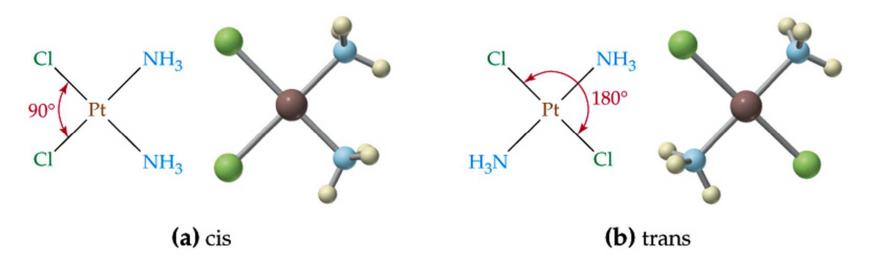


Such a transformation could be used as an energy storage device.



Stereoisomers

 Geometric Isomers of Pt(NH₃)₂Cl₂: In the cis isomer, atoms are on the same side. In the trans isomer, atoms are on opposite sides.



2.Stereoisomers

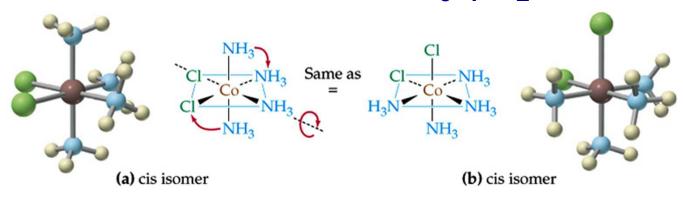
i. Diastereoisomers (geometric) have the same connections among atoms but different spatial orientations of the metal–ligand bonds.

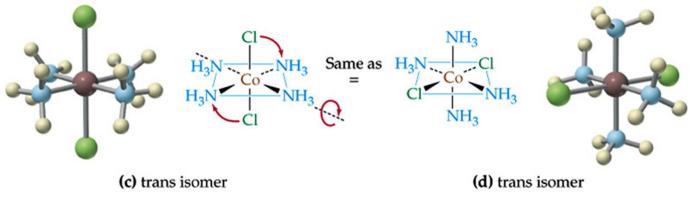
a) cis isomers have identical ligands in *adjacent corners* of a square.

b)trans isomers have identical ligands *across the corners* from each other.

Isomers

• Geometric Isomers of [Co(NH₃)₄Cl₂]CI:





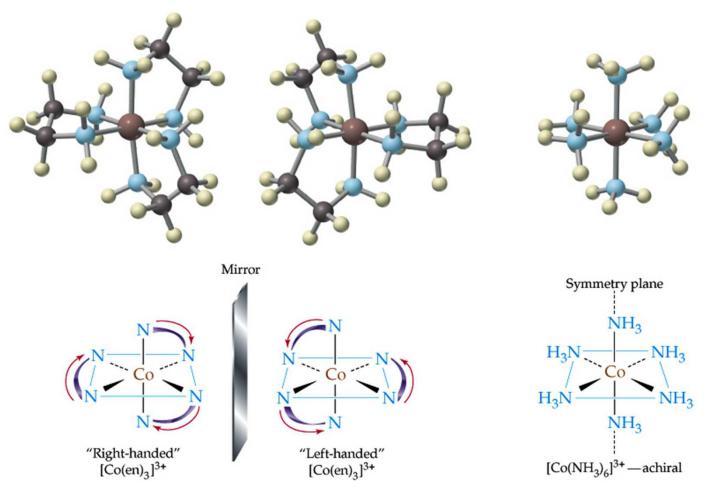
Chapter 20

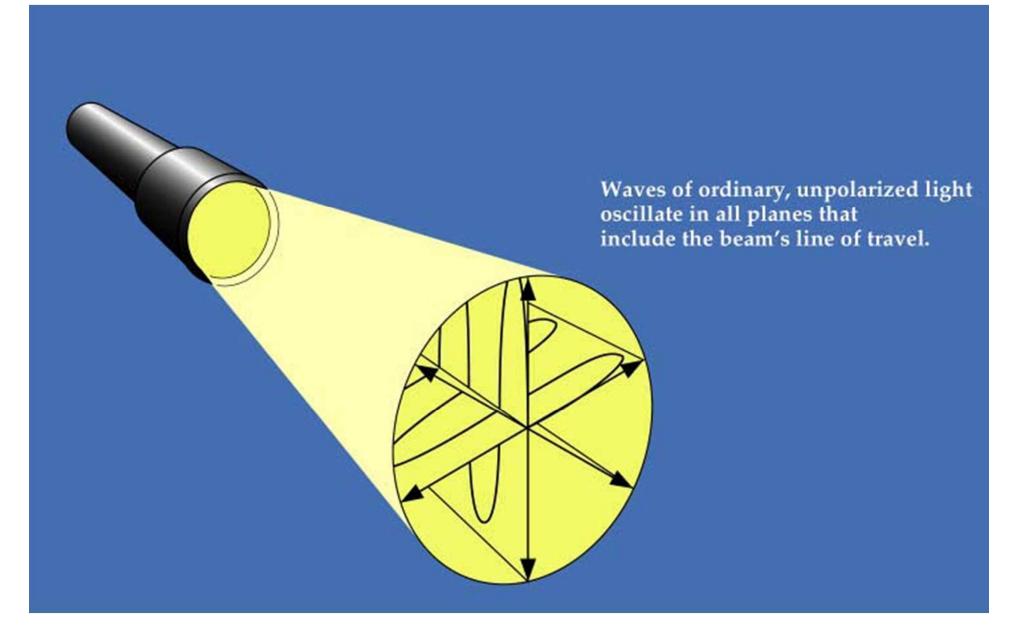
06

Enantiomers

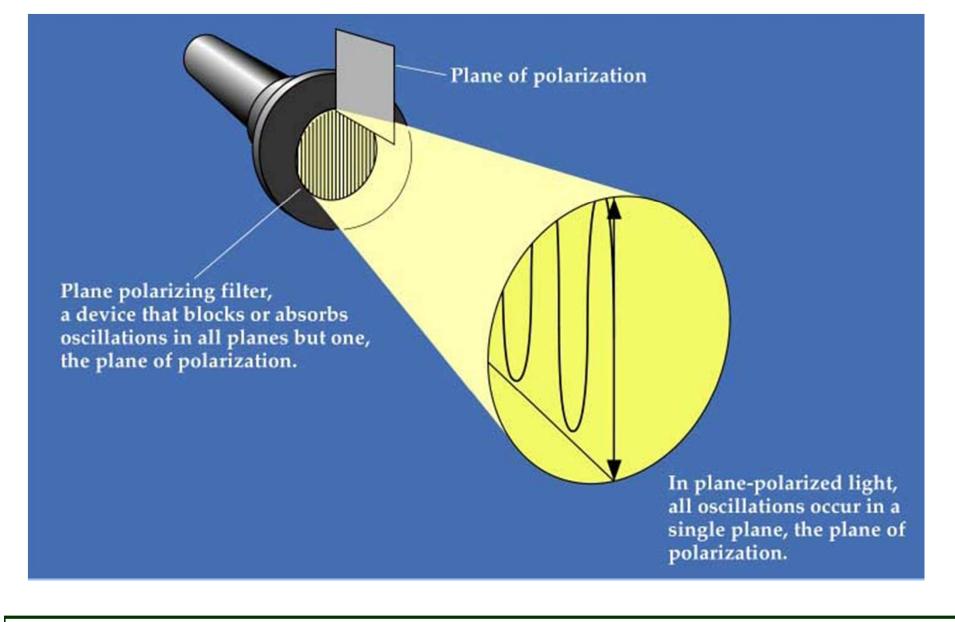
- Enantiomers are stereoisomers of molecules or ions that are *nonidentical mirror images* of each other.
- Objects that have "handedness" are said to be chiral, and objects that lack "handedness" are said to be achiral.
- An object or compound is *achiral* if it has a symmetry plane cutting through the middle.

Enantiomers

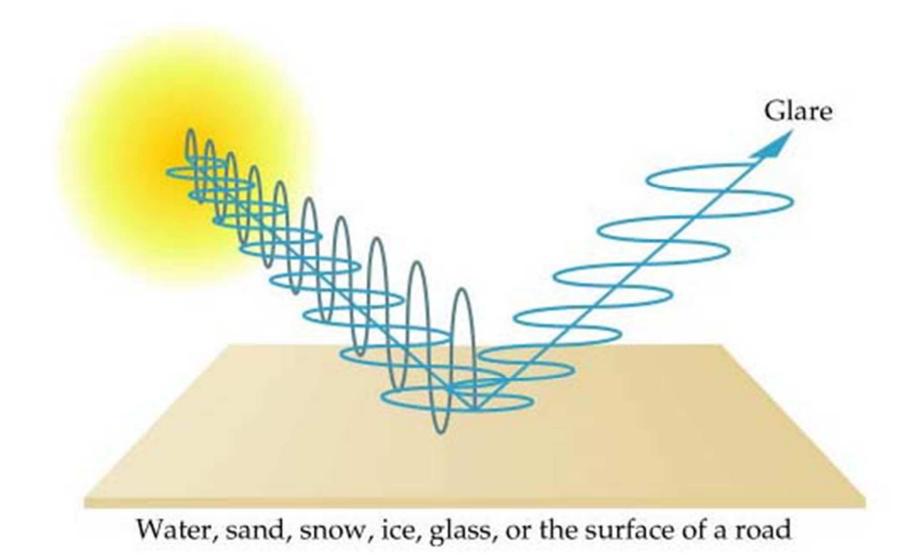




Unpolarized light.

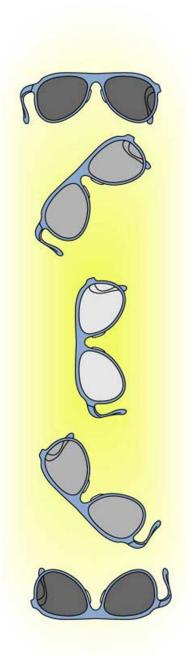


Plane-polarized light.



Reflected glare is plane-polarized light.

© 2003 John Wiley and Sons Publishers

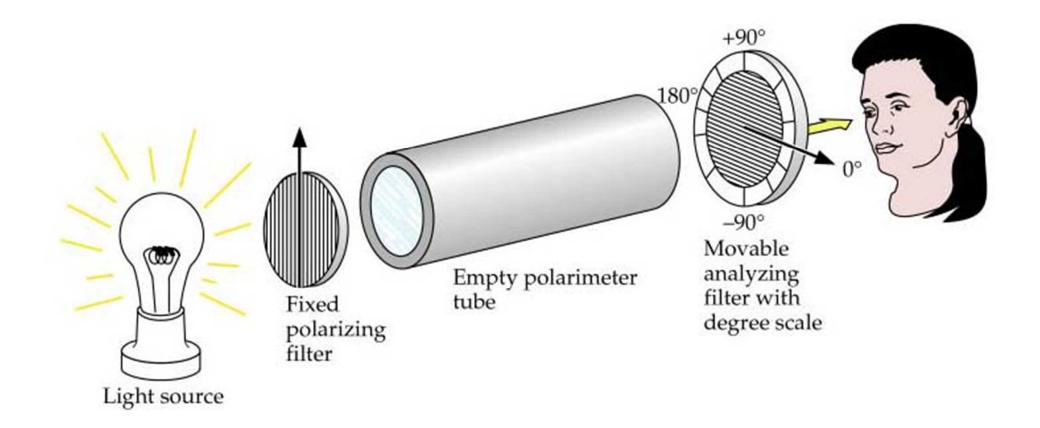


Polarizing sunglasses versus glare.



Courtesy Andy Washnik

The effect of polarizing lenses on unpolarized light.



Enantiomers

• Enantiomers have identical properties except for their reaction with other chiral substances and their effect on *plane-polarized light*.

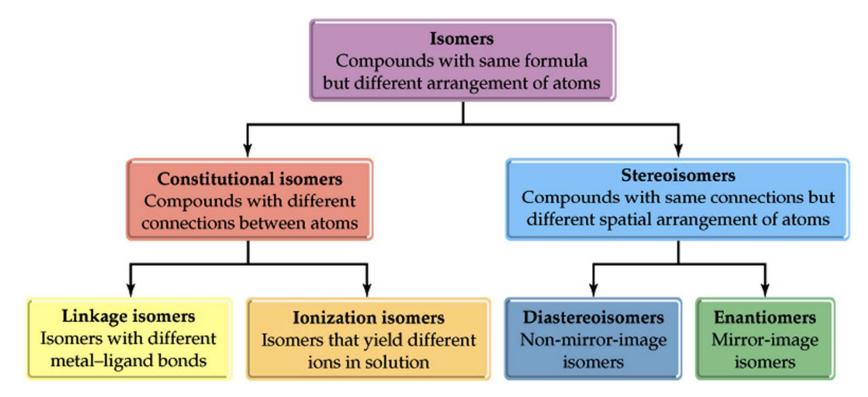
 Enantiomers are often called optical isomers; their effect on plane-polarized light can be measured with a polarimeter.

Enantiomers

- Plane-polarized light is obtained by passing ordinary light through a polarizing filter.
- In a polarimeter the plane-polarized light is passed though a chiral solution and the polarization plane measured with an analyzing filter.
 - If the plane rotates to the right it is *dextrorotatory*.
 - If the plane rotates to the left it is *levorotatory*.
 - Equal amounts of each are *racemic*.

Isomers

• **Isomers** are compounds that have the same formula but a different atomic arrangement.



Bonding in Complexes

• Bonding Theories attempt to account for the color and magnetic properties of transition metal complexes.

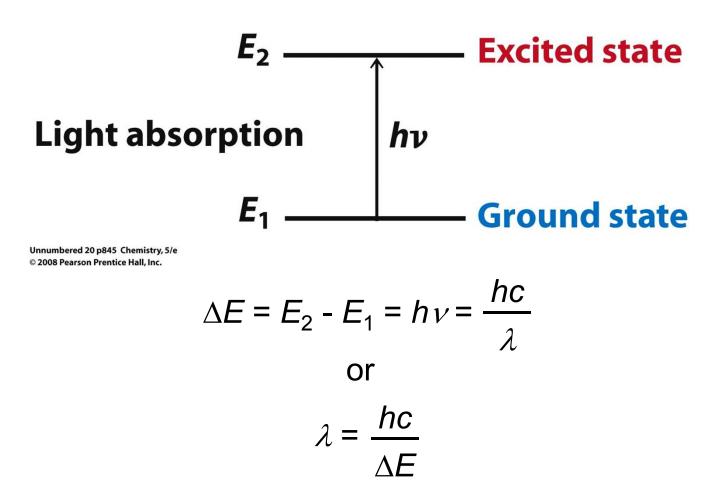




•Solutions of $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, & $[Ni(en)_3]^{2+}$

01

Color of Transition Metal Complexes



Color of Transition Metal Complexes

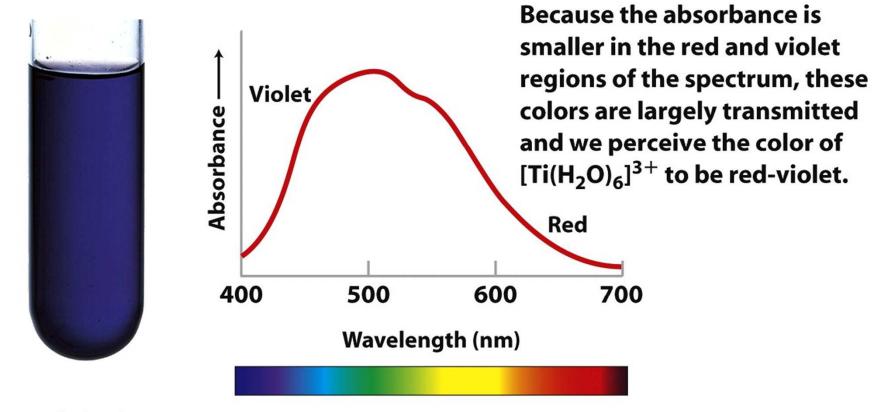


Figure 20-25 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

Color of Transition Metal Complexes

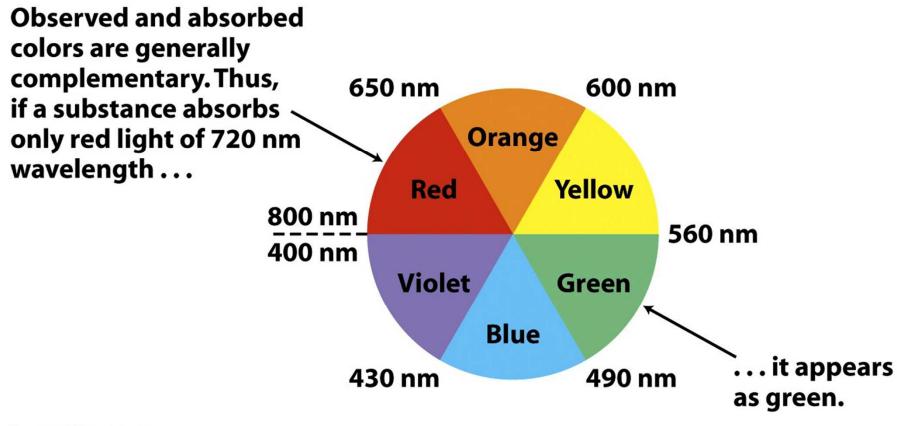


Figure 20-26 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

Bonding in Complexes: Valence Bond Theory





Unnumbered 20 p846 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

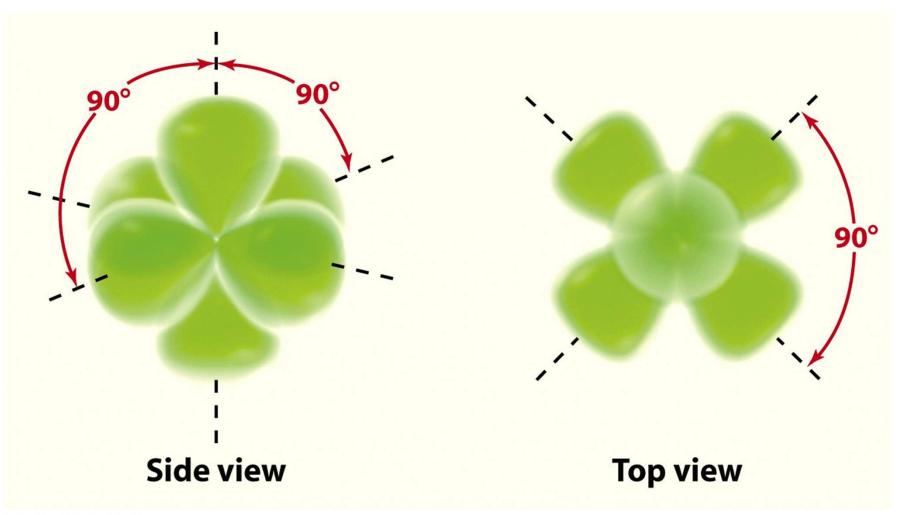
1 L 🧠

Occupied ligand atomic orbital



Coordinate covalent bond

The octahedral d²sp³ and sp³d²



Square Planar geometry of four dsp²

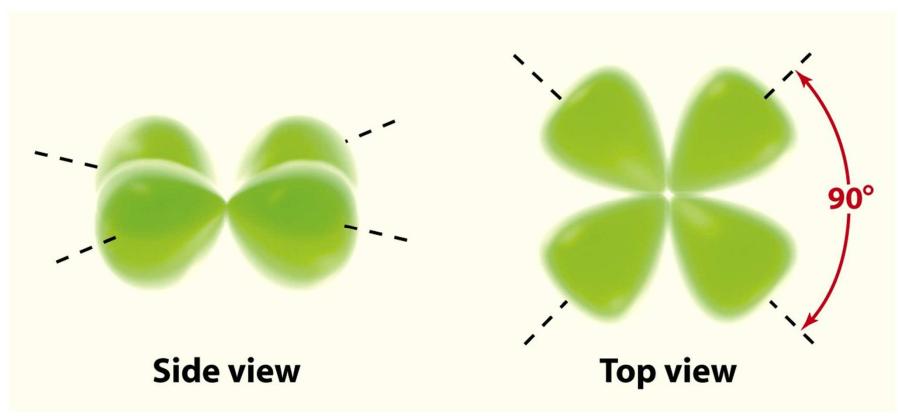


Figure 20-28 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

Bonding in Complexes: Valence Bond Theory

TABLE 20.7 Hybrid Orbitals for Common Coordination Geometries

Coordination Number	Geometry	Hybrid Orbitals	Example
2	Linear	sp	[Ag(NH ₃) ₂]⁺
4	Tetrahedral	sp ³	[CoCl₄] ^{2−}
4	Square planar	dsp ²	[Ni(CN) ₄] ^{2–}
6	Octahedral	d²sp³ or sp³d²	$[Cr(H_2O)_6]^{3+}, [Co(H_2O)_6]^{2+}$

Table 20-7 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

$$Co^{2+}: [Ar] \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{3d} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{4s} \frac{-}{4p}$$
Unnumbered 20 p847a Chemistry, 5/e
0 2008 Pearson Prentice Hall, Inc.
$$[CoCl_4]^{2-}: [Ar] \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{3d} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{4s} \stackrel{\uparrow}{4p} \stackrel{\uparrow}{4p} \frac{1}{4p}$$

$$Four sp^3 bonds to the ligands$$

Unnumbered 20 p847b Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

Bonding in Complexes: Valence Bond Theory

TABLE 20.7 Hybrid Orbitals for Common Coordination Geometries

Coordination Number	Geometry	Hybrid Orbitals	Example
2	Linear	sp	[Ag(NH ₃) ₂]⁺
4	Tetrahedral	sp ³	[CoCl₄] ^{2−}
4	Square planar	dsp ²	[Ni(CN) ₄] ²⁻
6	Octahedral	d²sp³ or sp³d²	$[Cr(H_2O)_6]^{3+}, [Co(H_2O)_6]^{2+}$

Table 20-7 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

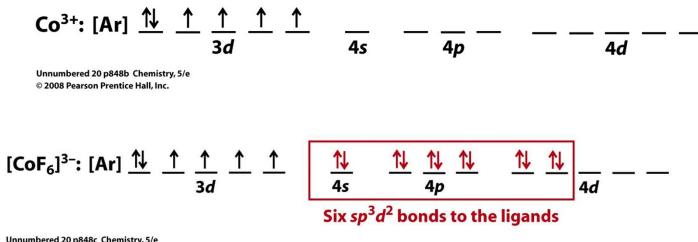
$$Ni^{2+}: [Ar] \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{3d} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{4s} \frac{}{4p}$$

$$Unnumbered 20 p847c Chemistry, 5/e
0 2008 Pearson Prentice Hall, Inc.
$$[Ni(CN)_{4}]^{2-}: [Ar] \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{3d} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{4s} \stackrel{\uparrow}{\longrightarrow} \stackrel{\uparrow}{4p} -$$

$$Four dsp^{2} bonds to the ligands$$$$

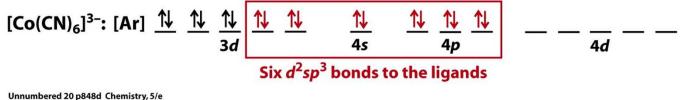
Unnumbered 20 p848a Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

High- and Low-Spin Complexes



Unnumbered 20 p848c Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

High spin: Maxium numer of unpaired electron, Paramagnetic



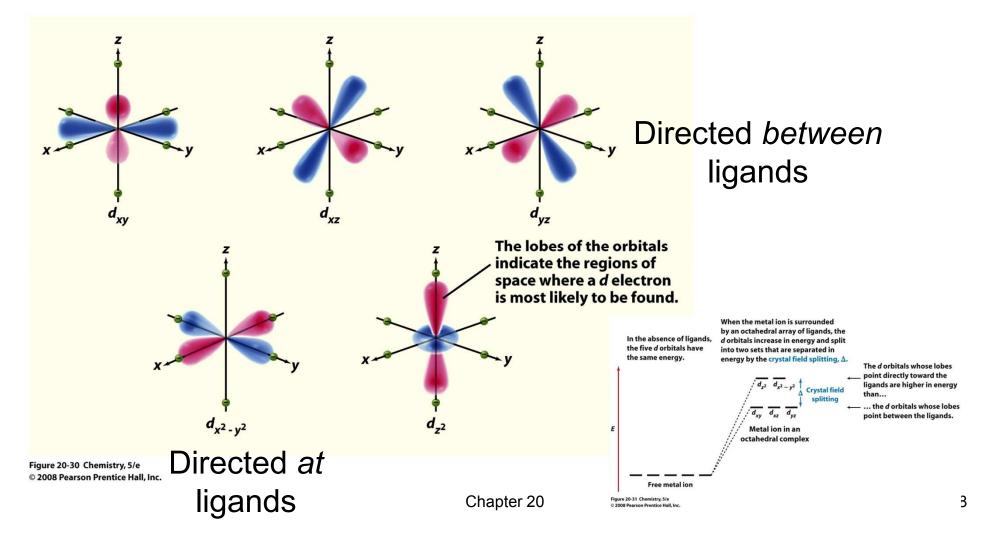
© 2008 Pearson Prentice Hall, Inc.

Low spin: Minimum numer of unpaired electron

Chapter 20

Crystal Field Theory: A model that views the bonding in complexes as arising from electrostatic interactions and considers the effect of the ligand charges on the energies of the metal ion *d* orbitals.

Octahedral Complexes



Octahedral Complexes

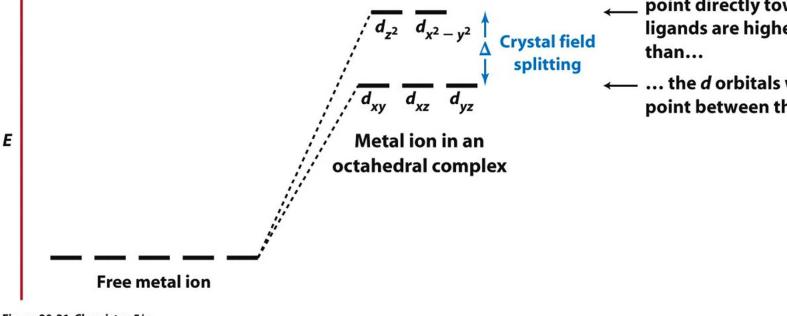
In the absence of ligands, the five d orbitals have the same energy.

When the metal ion is surrounded by an octahedral array of ligands, the d orbitals increase in energy and split into two sets that are separated in energy by the crystal field splitting, Δ .

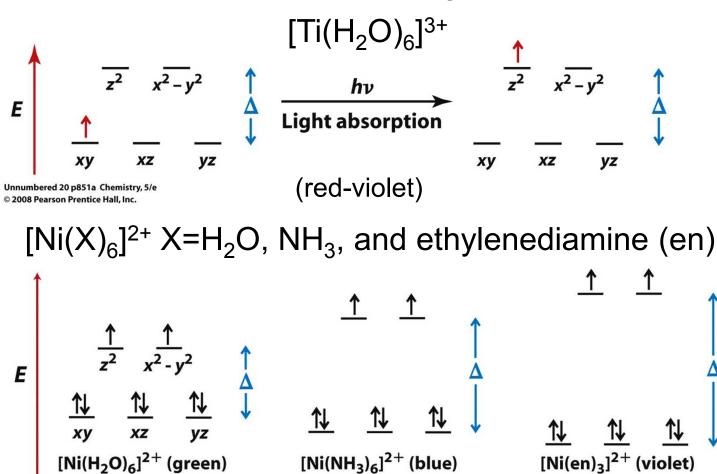
The *d* orbitals whose lobes point directly toward the ligands are higher in energy than...

the d orbitals whose lobes point between the ligands.

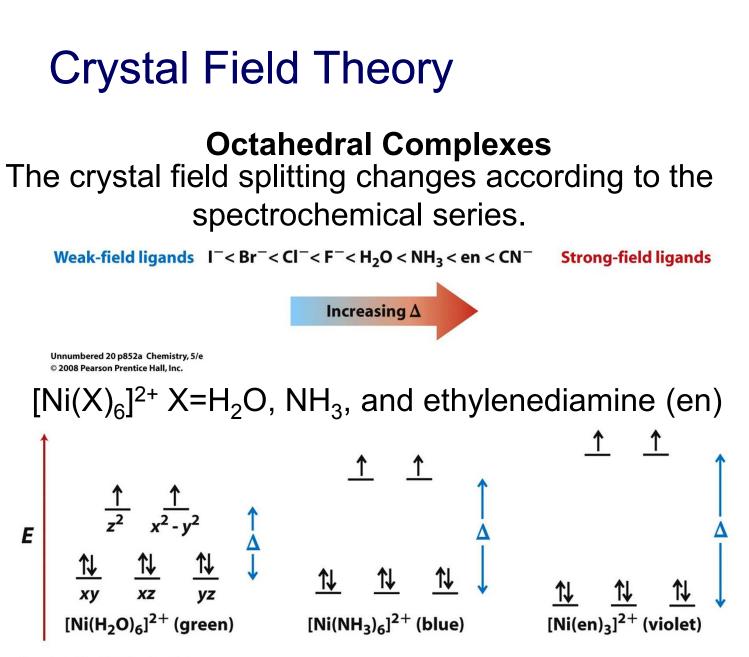
Figure 20-31 Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.



Octahedral Complexes



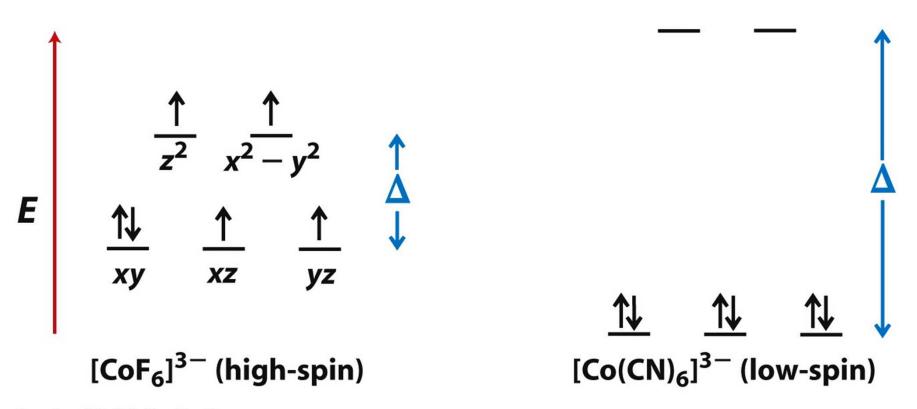
Unnumbered 20 p851b Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.



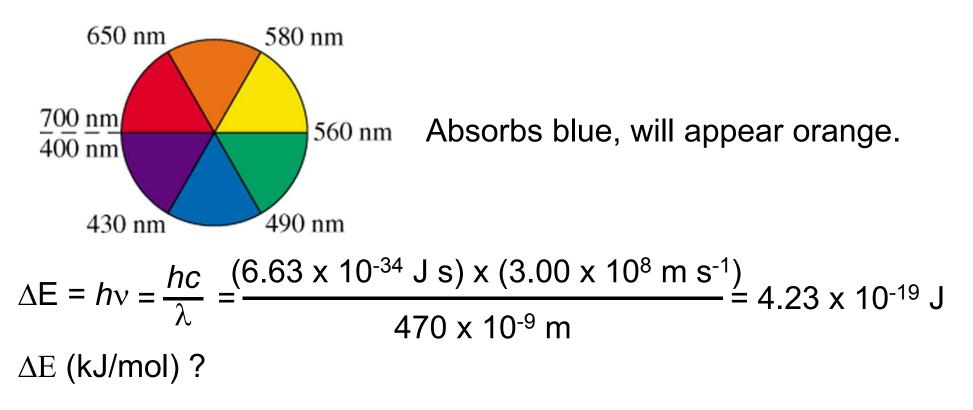
Unnumbered 20 p851b Chemistry, 5/e © 2008 Pearson Prentice Hall, Inc.

Octahedral Complexes

This accounts for the magnetic properties of complexes.



The absorption maximum for the complex ion $[Co(NH_3)_6]^{3+}$ occurs at 470 nm. What is the color of the complex and what is the crystal field splitting in kJ/mol?



4.23 x 10⁻¹⁹ J/atom x 6.022 x 10²³ atoms/mol = 255 kJ/mol