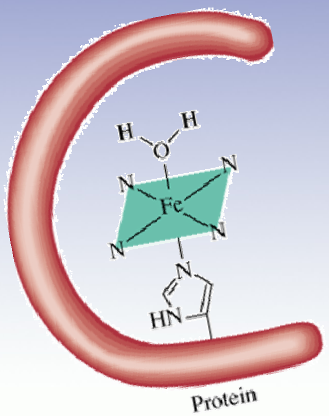
Chapter 21



Transition Metals and Coordination Chemistry

Chapter 21 Preview

Transition Metals and Coor. Chem.

- The Transition Metals: A survey

  General Properties, Electronic configuration, Oxidation states, Standard reduction potential, the 4th and 5th transition series

- The First-Row Transition Metals

  Coordination compounds, coordination numbers, ligands, nomenclature, structural and stereo-isomerism

- Bonding in Complex Ions

  Localized electron Model, Crystal field model, octahedral complexes and others

- Biologic Importance and Metallurgy

  Complexes, Iron and steel production, Heat treatment of steel

Introduction

- Transition metals (TMs) have many uses in our life: Iron, copper, titanium, silver, chromium, magnesium, Platinum…
- About 60 strategic and critical minerals are controlled by U. S. Government as they play a vital role in its economy and defense

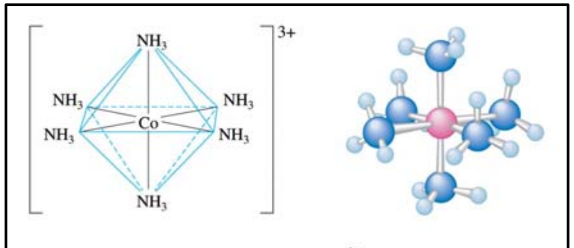
TABLE 21.1 Some Transition Metals Important to the U.S. Economy and Defense

Metal	Uses	Percentage Imported
Chromium	Stainless steel (especially for parts exposed to corrosive gases and high temperatures)	~91%
Cobalt	High-temperature alloys in jet engines, magnets, catalysts, drill bits	~93%
Manganese	Steelmaking	~97%
Platinum and	Catalysts	~87%

- Transition metal complex of iron provide for the transport and storage of oxygen
- Zinc is found in more than 150 biomolecules in humans …

21. 1 The Transition Metals: A Survey

- TMs show great similarities within a given period as well as within a given vertical groups.
- Inner d- and f-electrons cannot participate as easily in bonding as can s- and p-electrons.
- Ag is the best electrical and thermal conductor and copper the best second, thus copper is wide used in electrical systems and home facilities….others
- Their cations are often complex ions, where the ion is surrounded by a certain number as ligands.



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

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											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 I	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 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112	(113)	114	(115)	116	(117)	118

21. 1 The Transition Metals: A Survey

- Half- and complete- filled rule, see Cr and Cu electronic configuration is applied to first raw TMs mainly.
- Ionization electrons firstly takes place at the outer shell electrons, then the inner (n-1)d-orbitals to produce different oxidations states
- The common oxidation states of TMs is 2+ and the IE increases from Left-to-Right
- All metals except Cu can reduce H+ ions to hydrogen gas that increases from Left-to-Right
- 4d- and 5d-TMs are remarkably similar in size and used in special applications.

Electron Configurations and Other Properties of the First-Row Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electron configuration									
M	$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$
M^{2+}	—	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.9	1.9	1.9
Ionization energy (kJ/mol)									
First	631	658	650	652	717	759	760	736	745
Second	1235	1309	1413	1591	1509	1561	1645	1751	1958
Third	2389	2650	2828	2986	3250	2956	3231	3393	3578
Radius (pm)									
M	162	147	134	130	135	126	125	124	128
M^{2+}	—	90	88	85	80	77	75	69	72
M^{3+}	81	77	74	64	66	60	64	—	—
Standard reduction potential (V)*	−2.08	−1.63	−1.2	−0.74	−1.18	−0.44	−0.28	−0.25	0.34

*The half-reaction is $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ (except for Sc and Cr, where the ions are Sc^{3+} and Cr^{3+}, respectively).

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
				+7				
			+6	+6	+6			
		+5	+5	+5	+5			
	+4	+4	+4	**+4**	+4	+4		
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	+3
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**
								+1

(most stable oxidation numbers are shown in red)

21. 2 The First-row Transition Metals

- Sc is a rare element and not widely used but found in some electronics
- Ti is widely distributed in the crust (0.6%) and is excellent structural materials, e.g., jet engines and pumps. It is used in different forms, e.g., TiO2, TiCl4, …
- V is also widely spread (0.02%) and is mostly used in alloys and exists in different oxidation states.
- Cr is relatively rare and it is very important industrial materials, e.g., steel plating,.. Also exists in different oxidation states.
- Mn is abundant (0.1%) and used as essential materials of hard steel used for rock crushers
- Fe is the most abundant (4.7%) and most important to our civilization.
- Co…., Ni…., Cu….., Zn…..

TABLE 21.4 Oxidation States and Species for Vanadium in Aqueous Solution

Oxidation State of Vanadium	Species in Aqueous Solution
+5	VO_2^+ (yellow)
+4	VO^{2+} (blue)
+3	$V^{3+}(aq)$ (blue-green)
+2	$V^{2+}(aq)$ (violet)

TABLE 21.5 Typical Chromium Compounds

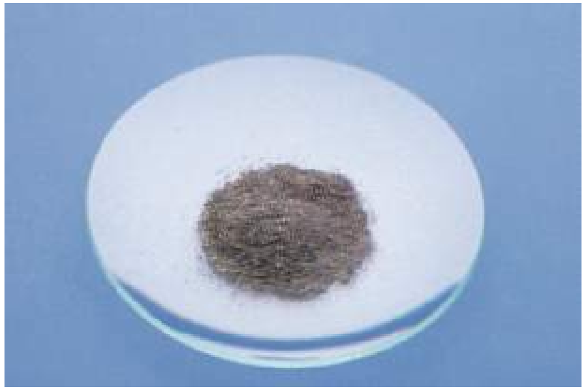
Oxidation State of Chromium	Examples of Compounds (X = halogen)
+2	CrX_2
+3	CrX_3
	Cr_2O_3 (green)
	$Cr(OH)_3$ (blue-green)
+6	$K_2Cr_2O_7$ (orange)
	Na_2CrO_4 (yellow)
	CrO_3 (red)

TABLE 21.6 Some Compounds of Manganese in Its Most Common Oxidation States

Oxidation State of Manganese	Examples of Compounds
+2	$Mn(OH)_2$ (pink)
	MnS (salmon)
	$MnSO_4$ (reddish)
	$MnCl_2$ (pink)
+4	MnO_2 (dark brown)
+7	$KMnO_4$ (purple)

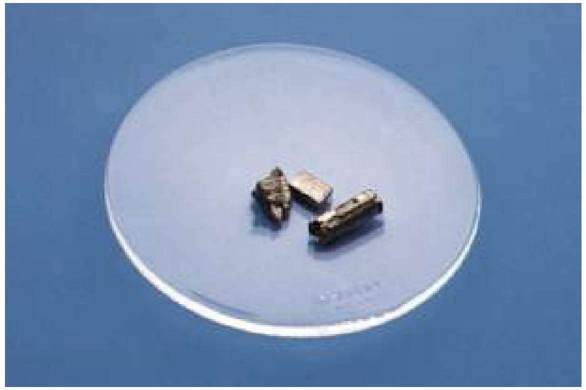
TABLE 21.7 Typical Compounds of Iron

Oxidation State of Iron	Examples of Compounds
+2	FeO (black)
	FeS (brownish black)
	$FeSO_4 \cdot 7H_2O$ (green)
	$K_4Fe(CN)_6$ (yellow)
+3	$FeCl_3$ (brownish black)
	Fe_2O_3 (reddish brown)
	$K_3Fe(CN)_6$ (red)
	$Fe(SCN)_3$ (red)
+2, +3 (mixture)	Fe_3O_4 (black)
	$KFe[Fe(CN)_6]$ (deep blue, "Prussian blue")



Scandium

Titanium



Vanadium

Chromium

Manganese

Iron

Cobalt

Nickel

Copper

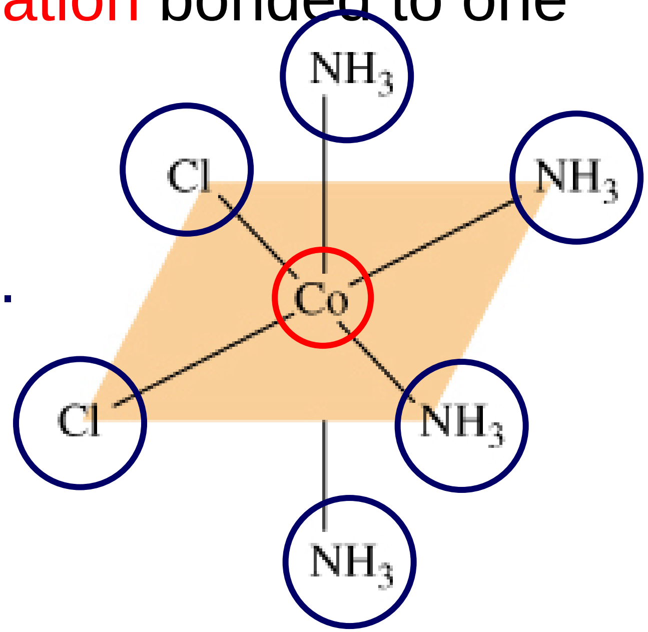
21.3 Coordination Compounds

A ***coordination compound*** typically consists of a complex ion and a counter ion.

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

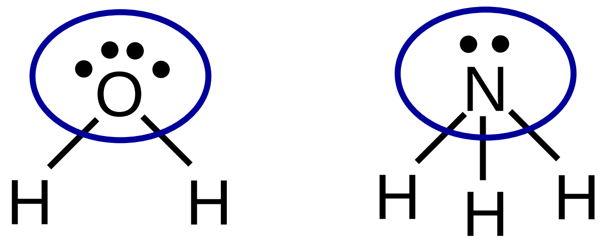
The molecules or ions that surround the metal in a complex ion are called ***ligands***.

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



21.3 Coordination Compounds

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



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

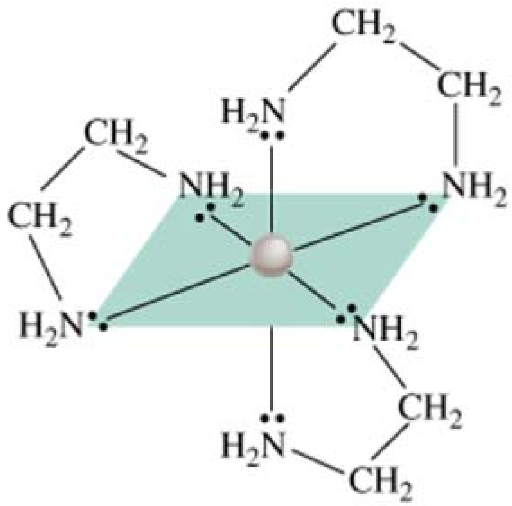
<u>Ligands with:</u>

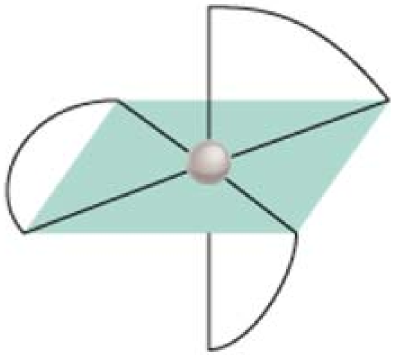
one donor atom	monodentate	H_2O, NH_3, Cl^-
two donor atoms	bidentate	ethylenediamine
three or more donor atoms	polydentate	EDTA

21.3 Coordination Compounds

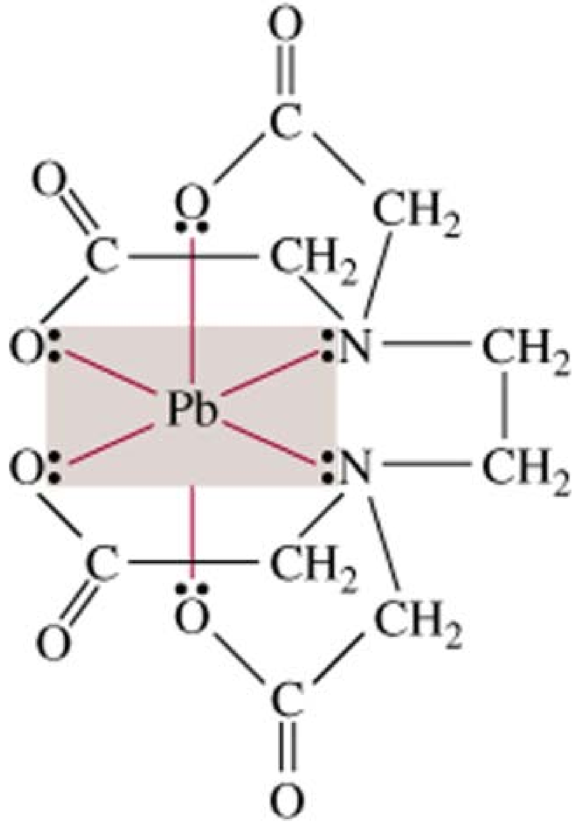
bidentate ligand

$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$





polydentate ligand (EDTA)



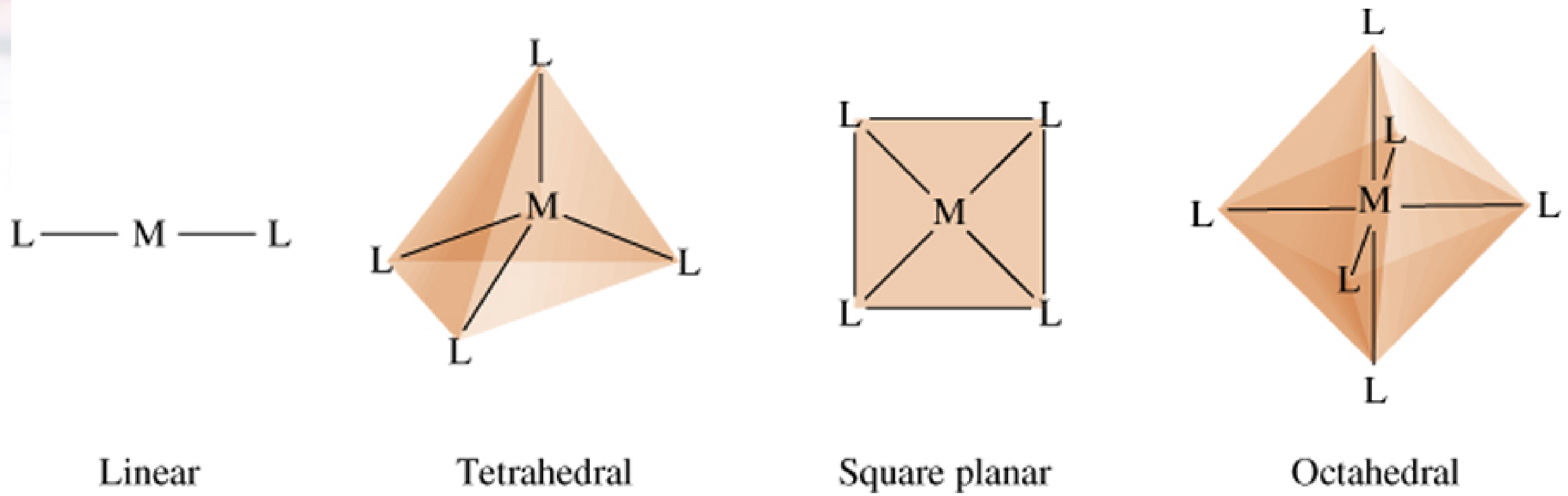
Bidentate and polydentate ligands are called ***chelating agents***

Common coordination numbers and classes of ligands

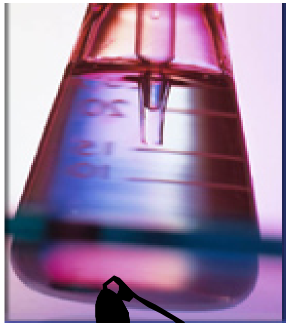
TABLE 21.12 Typical Coordination Numbers for Some Common Metal Ions

M^+	Coordination Numbers	M^{2+}	Coordination Numbers	M^{3+}	Coordination Numbers
Cu^+	2, 4	Mn^{2+}	4, 6	Sc^{3+}	6
Ag^+	2	Fe^{2+}	6	Cr^{3+}	6
Au^+	2, 4	Co^{2+}	4, 6	Co^{3+}	6
		Ni^{2+}	4, 6		
		Cu^{2+}	4, 6	Au^{3+}	4
		Zn^{2+}	4, 6		

21.3 Coordination Compounds



Coordination number	Structure
2	Linear
4	Tetrahedral or Square planar
6	Octahedral



21.3 Coordination Compounds

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

NH_3 has no charge

? Cr + 6x(0) + 3x(-1) = 0

Cr = +3

QUESTION

Ethylenediamine (en) is a bidentate ligand. What is the coordination number of cobalt in $[Co(en)_2Cl_2]Cl$?

1) four
2) five
3) seven
4) eight
5) six

Species found outside of the brackets are not directly bonded to the metal ion.

Naming Coordination Compounds

$[Cr(H_2O)_4Cl_2]Cl$

- The cation is named before the anion.
- Within a complex ion, the ligands are named first **in alphabetical order** and the metal atom is named last.
- The names of anionic ligands end with the letter *o*. Neutral ligands are usually called by the name of the molecule. The exceptions are H_2O (aquo), CO (carbonyl), and NH_3 (ammine).
- When several ligands of a particular kind are present, the Greek prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* are used to indicate the number. If the ligand contains a Greek prefix, use the prefixes *bis*, *tris*, and *tetrakis* to indicate the number.
- The oxidation number of the metal is written in Roman numerals following the name of the metal.
- If the complex is an anion, its name ends in *–ate*.

Common Names

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

Names of Common Ligands in Coordination Compounds

Ligand	Name of Ligand in Coordination Compound
Bromide, Br^-	Bromo
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Hydroxide, OH^-	Hydroxo
Oxide, O^{2-}	Oxo
Carbonate, CO_3^{2-}	Carbonato
Nitrite, NO_2^-	Nitro
Oxalate, $C_2O_4^{2-}$	Oxalato
Ammonia, NH_3	Ammine
Carbon monoxide, CO	Carbonyl
Water, H_2O	Aquo
Ethylenediamine	Ethylenediamine
Ethylenediaminetetraacetate	Ethylenediaminetetraacetato

QUESTIONS

What is the systematic name of
$[Cr(H_2O)_4Cl_2]Cl$?

tetraaquodichlorochromium(III) chloride

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

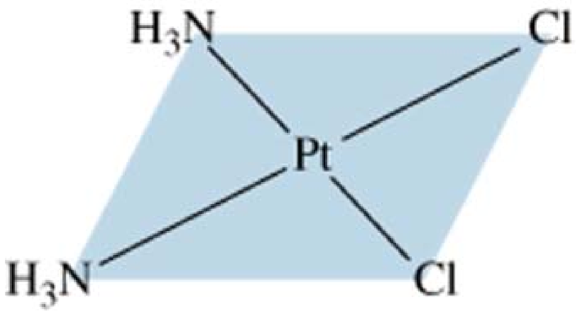
$[Co(en)_3]SO_4$

21.4 Isomerism

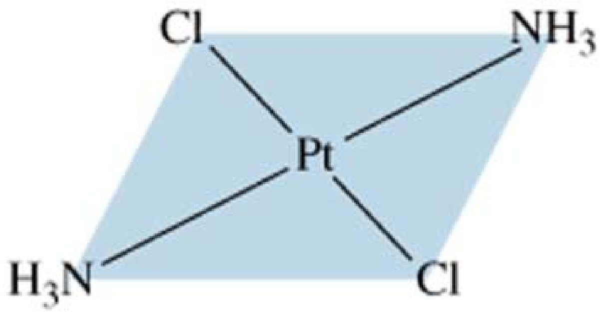
Two or more species have the same formula but different properties are called ***isomers***.

Stereoisomers are compounds that are made up of the same types and numbers of atoms bonded together in the same sequence but with different spatial arrangements.

Geometric isomers are stereoisomers that cannot be interconverted without breaking a chemical bond.



cis-$[Pt(NH_3)_2Cl_2]$



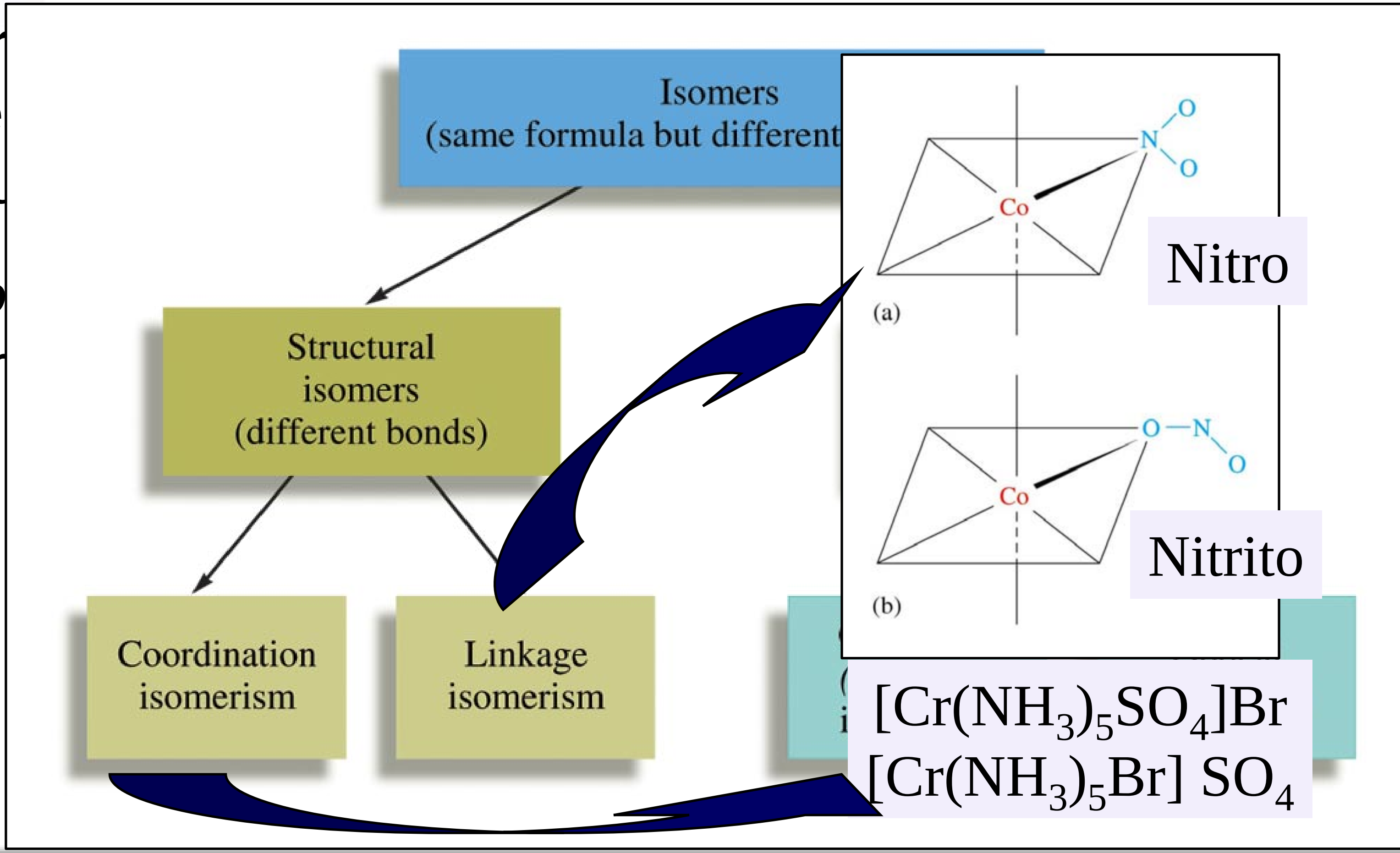
trans-$[Pt(NH_3)_2Cl_2]$

21.4 Isomerism

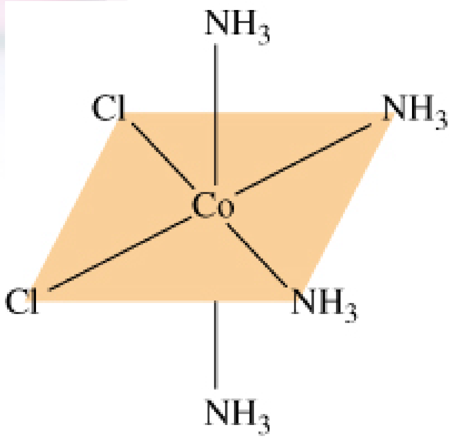
Two or more species have the same formula but different properties are called ***isomers***.

Ster ... ame
type
sequ

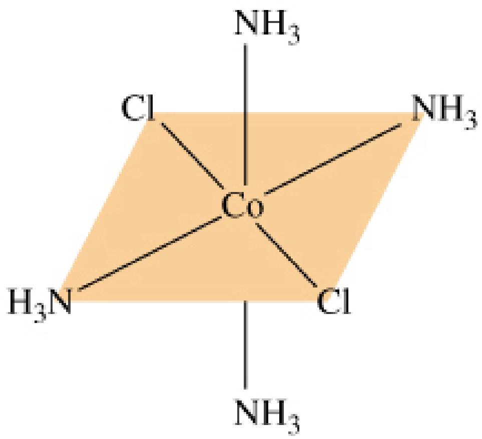
Geo
inter



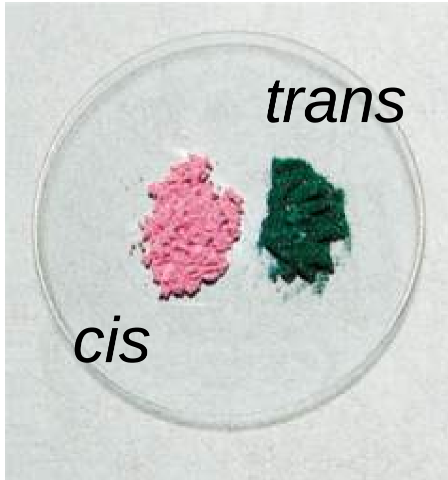
QUESTION



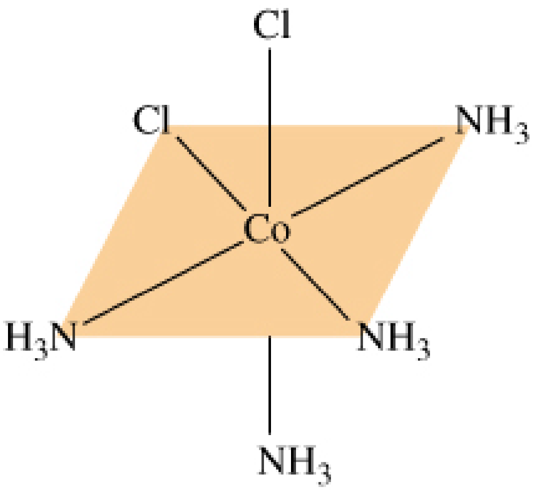
cis-$[Co(NH_3)_4Cl_2]$

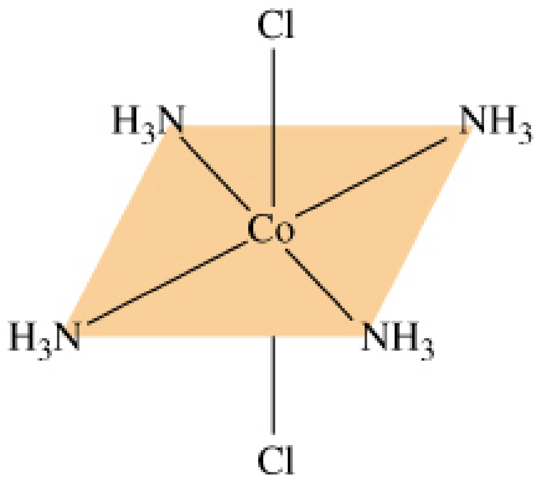


trans-$[Co(NH_3)_4Cl_2]$



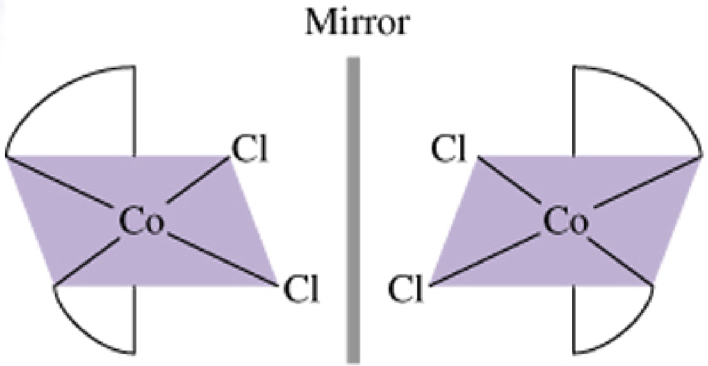
Are these additional geometric isomers of $[Co(NH_3)_4Cl_2]$?

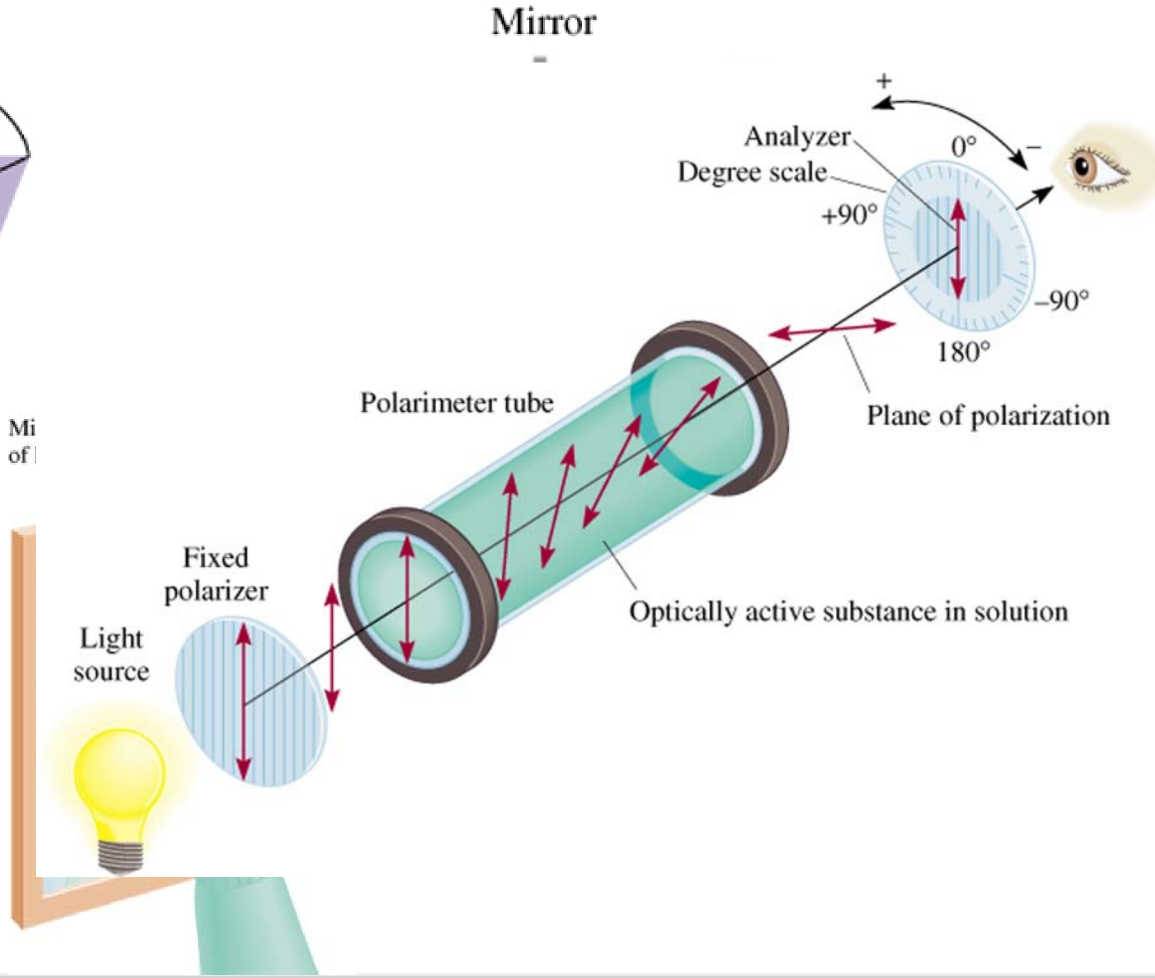




21.4 Isomerism

Optical isomers are nonsuperimposable mirror images.





cis-$[Co(en)_2Cl_2]$

Optically active

enantiomers

Chiral

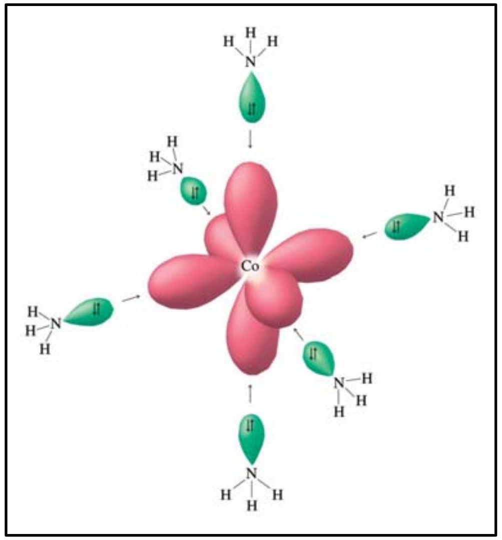
Dextro- or levo-rotatory

21.5 Bonding in Complex Ions: The localized Electron Model

Same model used for the formation os the hybrid atomic orbital using VSEPR rule however:

1. It cannot account for the square planar complex
2. The interaction beteen metal ion and ligand can be viewed as a lewis acid-base

A Set of d2sp3 Hybrid Orbitals on Co^{3+} can Accept as an Electron Pair from each of Six NH_3 Ligands to Form the $Co(NH_3)_6^{3+}$ Complex Ion

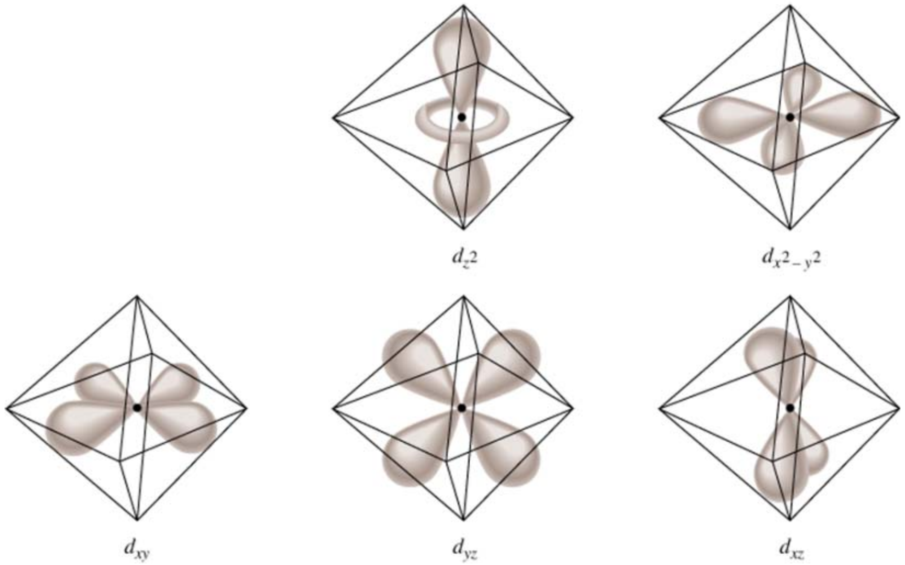


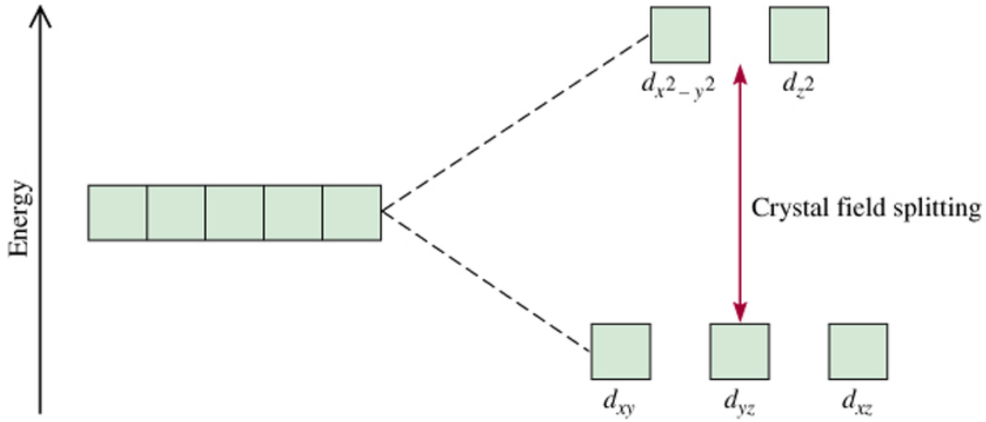
It is not generally used because it also cannot account for the magnetism

21.6 The crystal Field Model

The localized model cannot account for the complex properties because it did not indicated how the energies of d-orbitals are affected by complex ion formation.

The crystal field model focuses on the d-orbital energies, e.g., octahedral complexes

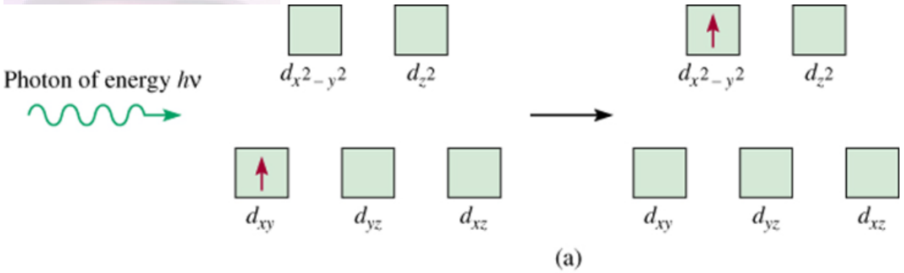




All equal in energy **in the absence of ligands!**

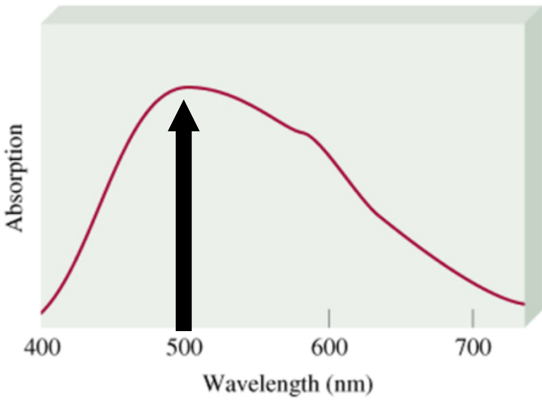
Crystal field splitting (Δ) is the energy difference between two sets of d orbitals in a metal atom when ligands are present

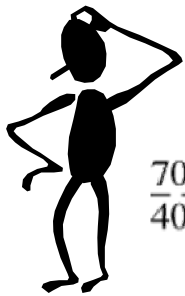
21.6 Crystal field Model

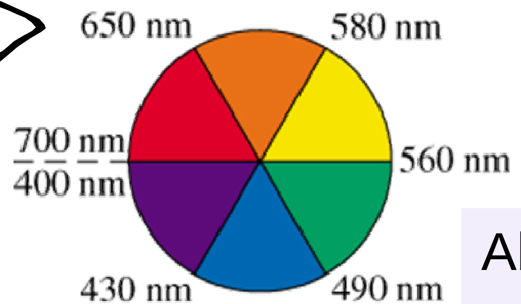


The absorption maximum for the complex ion $[Co(NH_3)_6]^{3+}$ occurs at 470 nm. What is the color of the complex and what is the crystal field splitting in kJ/mol?

$$\Delta = h\nu = \frac{hc}{\lambda}$$







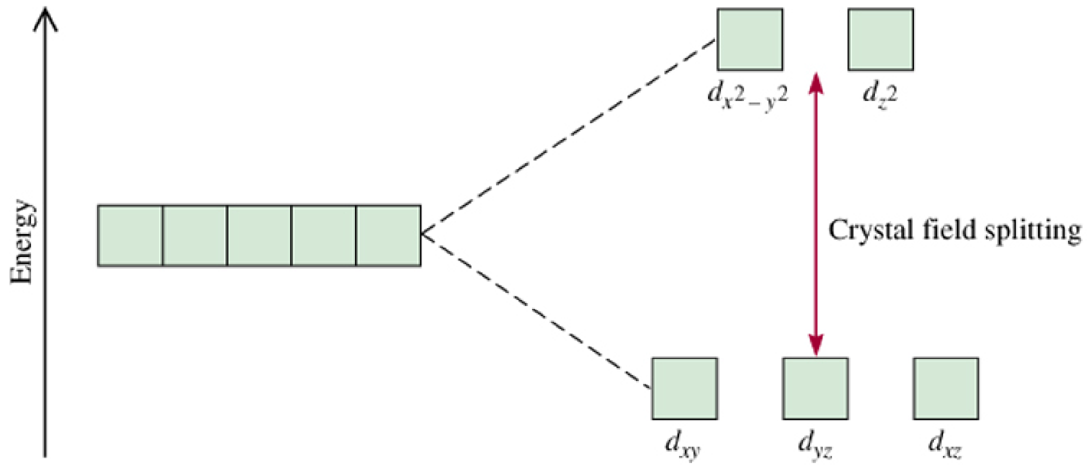
Absorbs blue,
will appear orange.

$$\Delta = h\nu = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34}\ \text{J s}) \times (3.00 \times 10^{8}\ \text{m s}^{-1})}{470 \times 10^{-9}\ \text{m}} = 4.23 \times 10^{-19}\ \text{J}$$

$$\Delta = 4.23 \times 10^{-19}\ \text{J/atom} \times 6.022 \times 10^{23}\ \text{atoms/mol} = 255\ \text{kJ/mol}$$

21.6 Crystal field Model

Spectrochemical Series

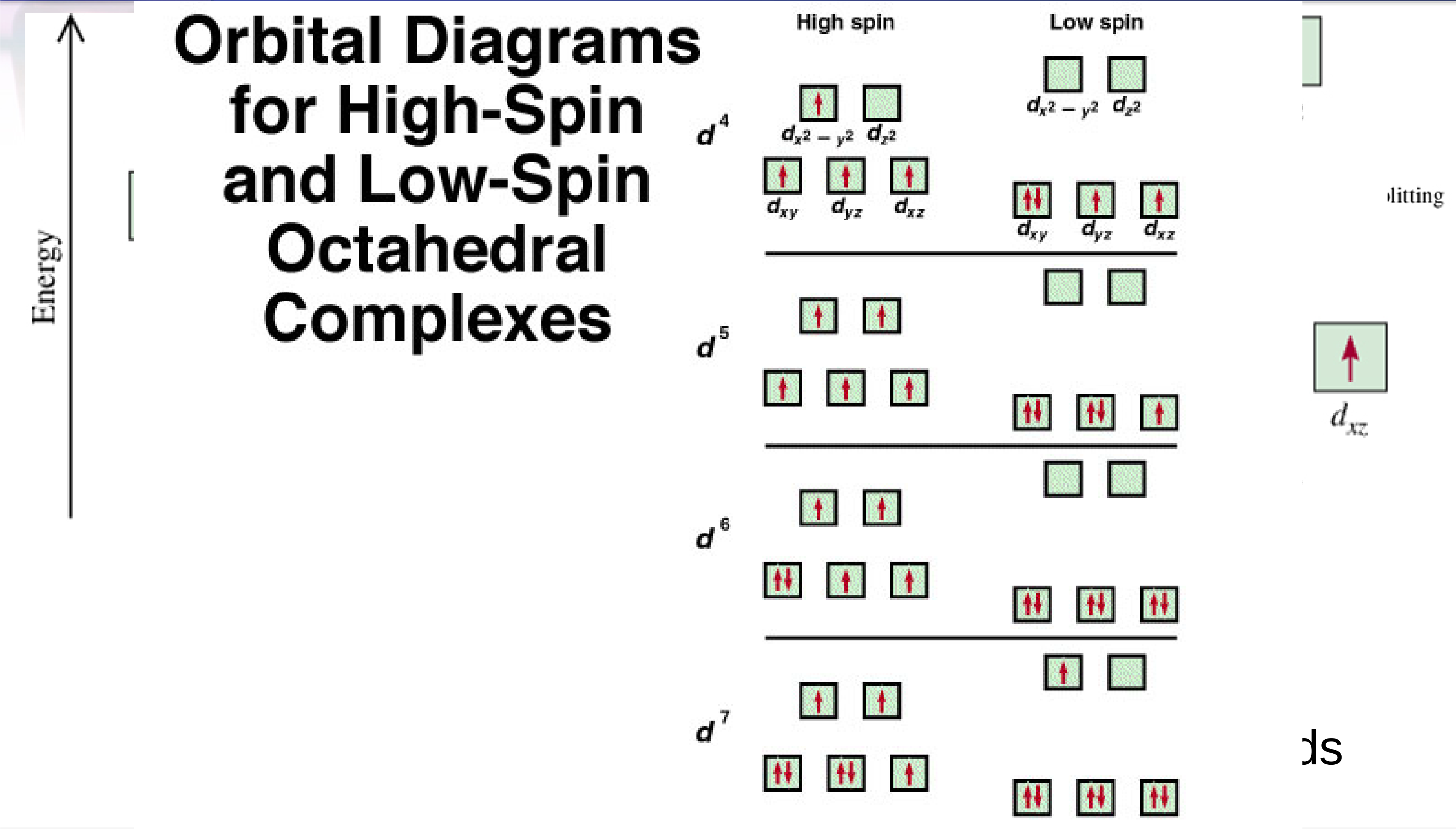


$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < CN^- < CO$

Weak field ligands
Small Δ

Strong field ligands
Large Δ

21.6 Crystal field Model



QUESTION

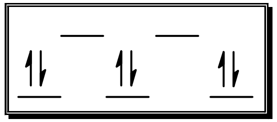
Which of the following is paramagnetic?

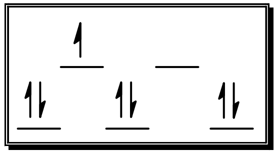
1) $Zn(H_2O)_6^{2+}$
2) $Co(NH_3)_6^{3+}$ (strong field)
3) $Cu(CN)_3^{2-}$
4) $Mn(CN)_6^{2-}$ (strong field)
5) None of these

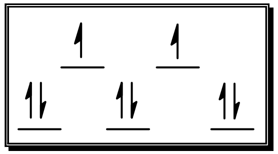
In a strong field Mn^{3+} has 3 electrons in three half-filled orbitals.

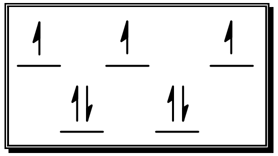
QUESTION

Which of the following crystal field diagrams is correct for $Co(CN)_6^{4-}$ where CN^- is a strong field ligand?

1) 

2) 

3) 

4) 

5) none of these

Strong field splitting indicates that the lowest three orbitals are filled before the seventh electron is placed in a higher orbital.

21.6 Crystal field Model

Figure 21.27 The Crystal Field Diagrams for Octahedral and Tetrahedral Complexes

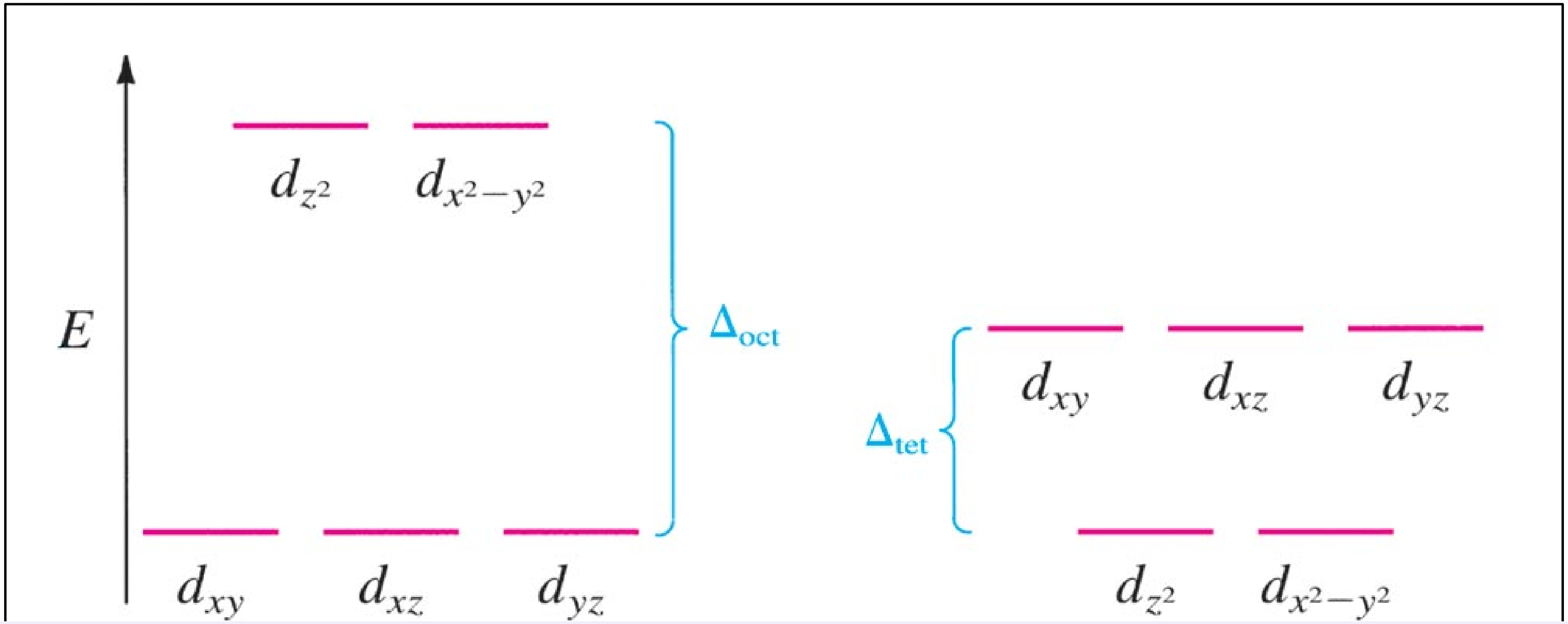


Figure 21.28 a-b (a) The Crystal Field Diagram for a Square Planar Complex Oriented in the xy Plane with Ligands along the x and y Axes (b) The Crystal Field Diagram for a Linear Complex where the Ligands Lie along the z Axis

21.6 Crystal field Model

Figu
Octa

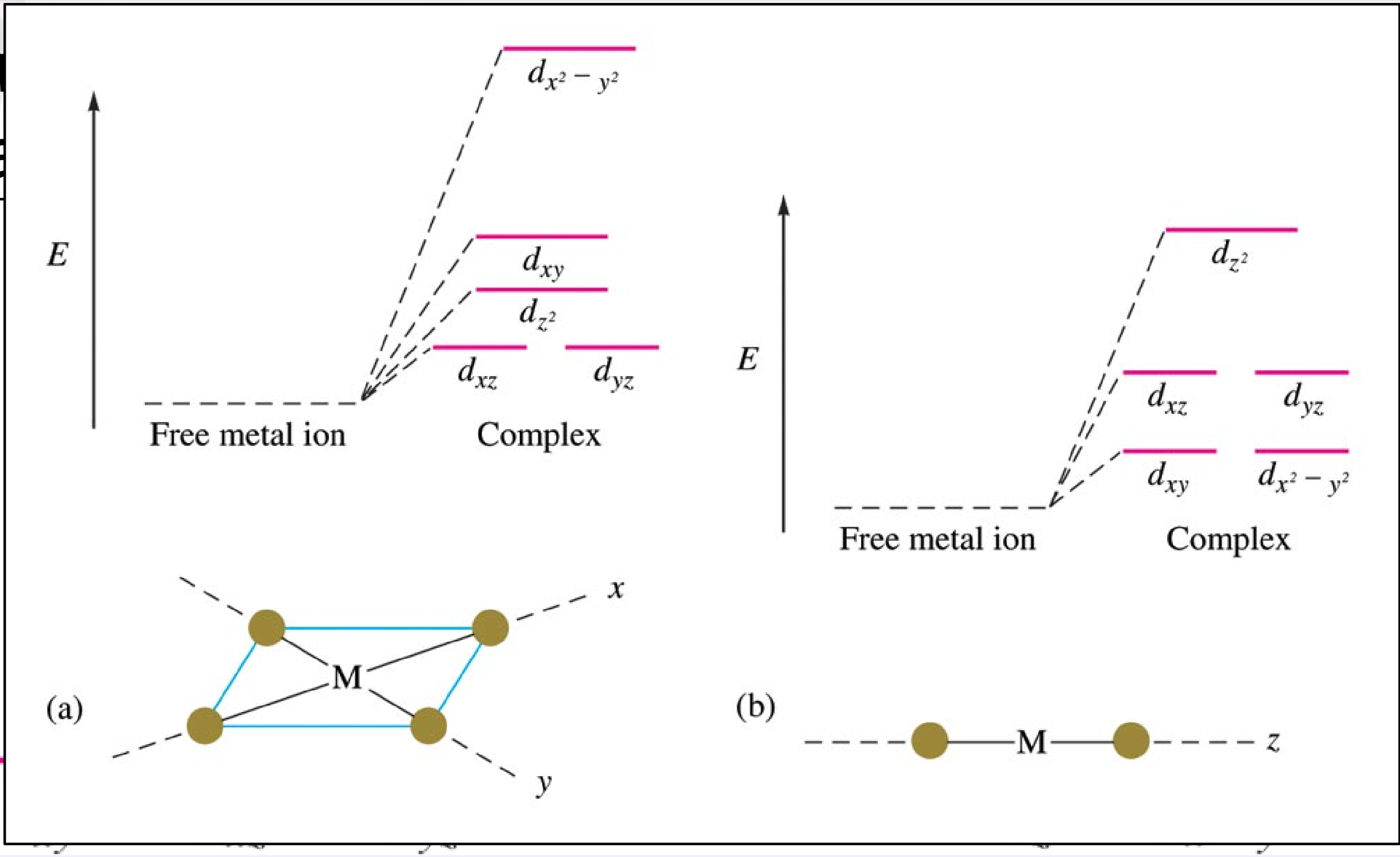
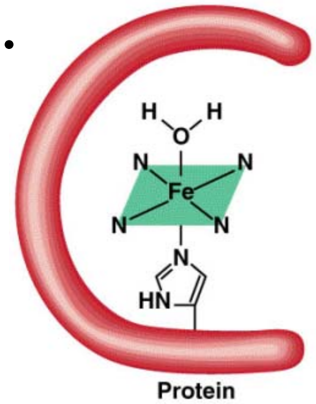


Figure 21.28 a-b (a) The Crystal Field Diagram for a Square Planar Complex Oriented in the xy Plane with Ligands along the x and y Axes (b) The Crystal Field Diagram for a Linear Complex where the Ligands Lie along the z Axis

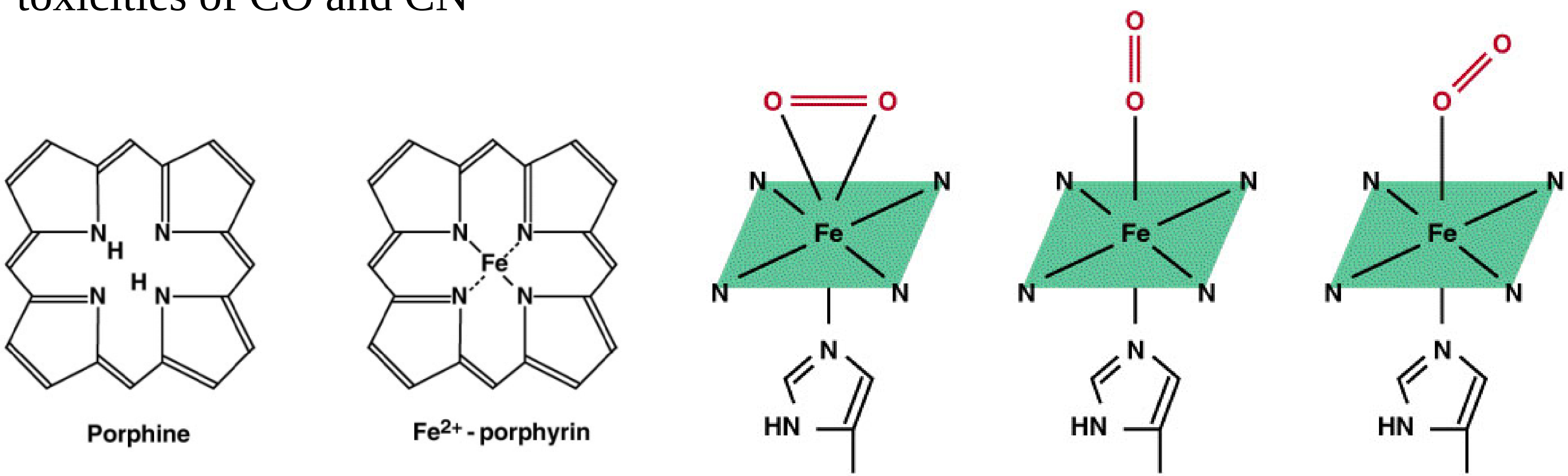
21.7 Biologic Importance

Iron plays a central role in almost all living cells.

- Cytochromes are the basic unit in respiratory chain
- Cytochromes consists of iron-complex (heme) and protien
- Heme contains Fe^{2+} coordinated to porphyrin (tetradentate)



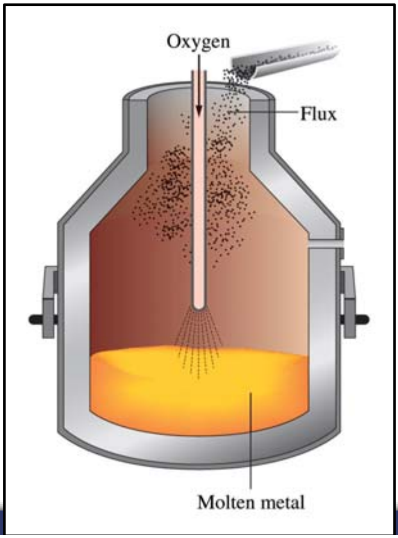
- Oxygen stored in a molecule called Myoglobin
- Understanding of biologic role of iron allows to explain the toxicities of CO and CN^{-}



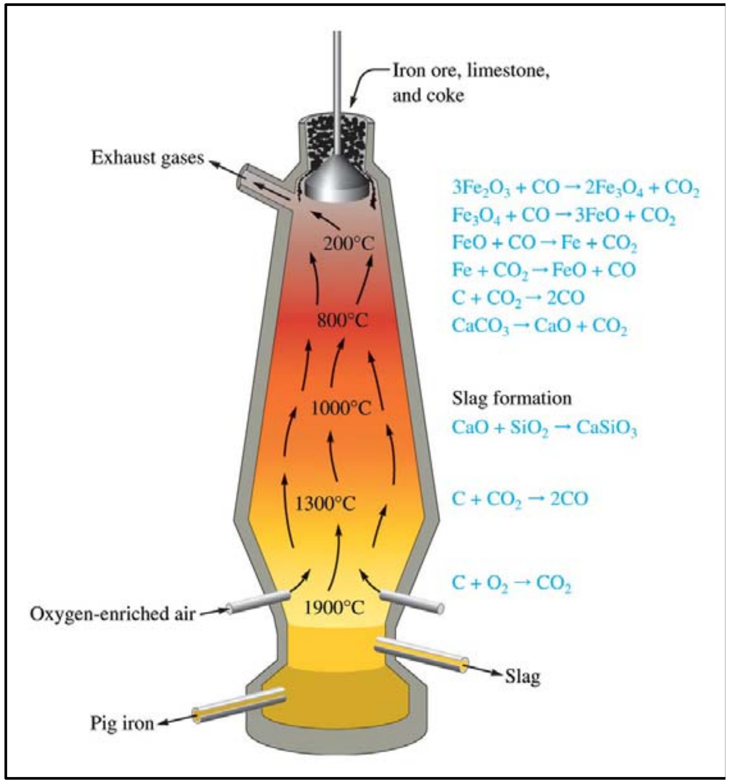
21.8 Metallurgy and Iron and Steel Production

The major steps in metallurgy are:

- Mining
- Pretreatment of the ore
- Reduction to the free metal
- Purification of the metal (refining)
- Alloying



The Basic Oxygen Process for Steelmaking



The Blast Furnace used in the Production of Iron