Chapter 20: Transition Metals and Coordination Chemistry

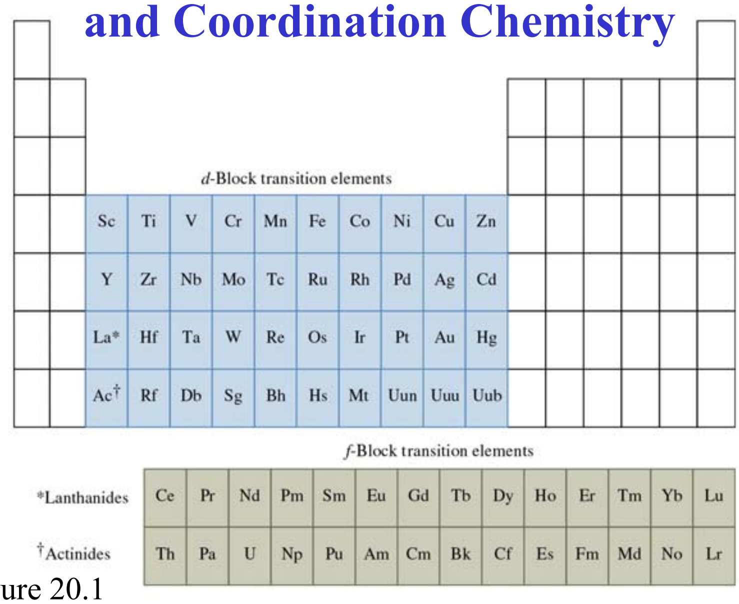


Figure 20.1

Chapter 20: Transition Metals and Coordination Chemistry

20.1 Survey of transition metals
20.2 1st-row transition metals
20.3 Coordination compounds
20.4 Isomerism
20.5 Bonding in complex ions: The localized electron model
20.6 The crystal field model
20.7 The molecular orbital model
20.8 The biological importance of coordination complexes

General Properties of Transition metals:

- metallic luster
- high electrical and thermal conductivity
- wide range of melting points (e.g. W @ 3400°C, Hg <25°C) and hardness
- wide range of reactivity toward O_2
  - Fe_2O_3 - rust
  - Fe_3O_4 - *magnetite*- magnetic recording material
  - Oxides of Cr, Co, and Ni- very hard
  - Coinage metals (Au, Ag, Pt, Pd) do not react readily with O_2

Some important aspects of transition metal ions:

1. The valence electrons are in d orbitals

2. The d orbitals do not have large radial extension

3. The d orbitals are therefore *mostly* nonbonding in complexes of transition metal ions

For these reasons, the effects of redox changes are substantially smaller for transition metals than for main group elements

Review Section 12.13!

Radial distribution functions

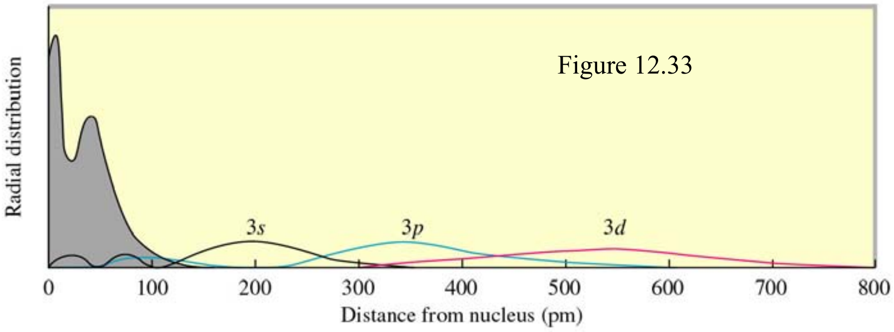


Figure 12.33

Representation of the 3*d* orbitals

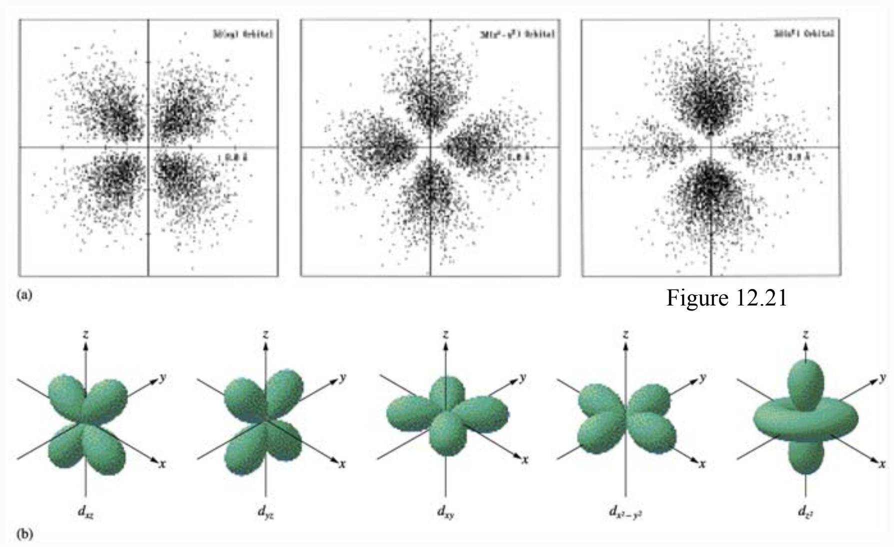


Figure 12.21

Radial probability of 3d vs. 4s orbitals

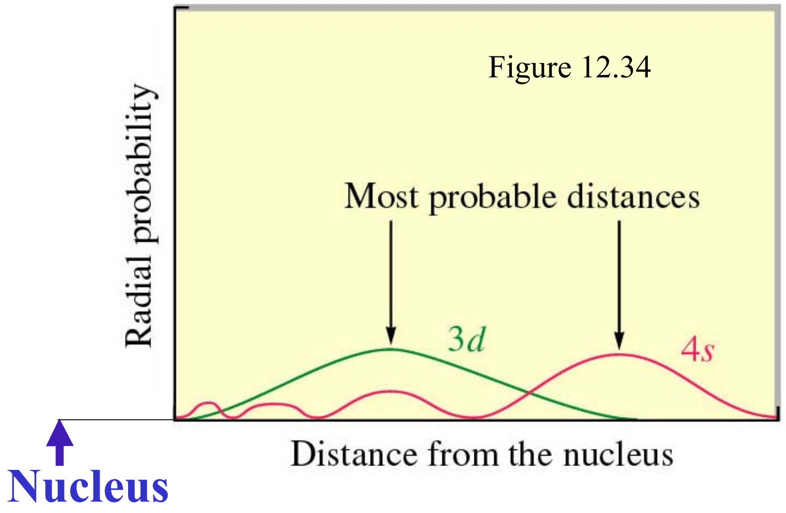
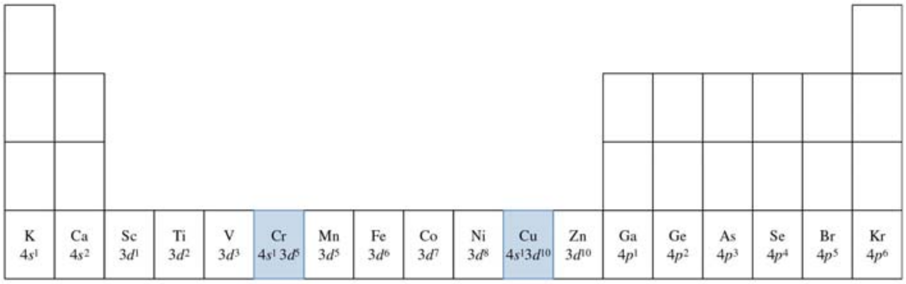


Figure 12.34

Electron configurations of the *neutral* transition metal elements



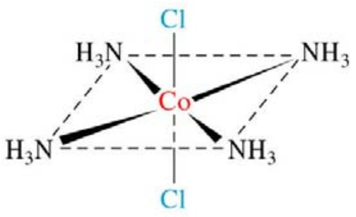
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
$4s^1$	$4s^2$	$3d^1$	$3d^2$	$3d^3$	$4s^1 3d^5$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$4s^1 3d^{10}$	$3d^{10}$	$4p^1$	$4p^2$	$4p^3$	$4p^4$	$4p^5$	$4p^6$

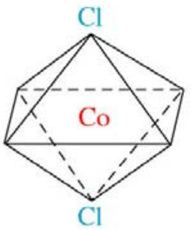
Figure 12.27

More General Properties of Transition Metals:

- Easily oxidized
- Readily form ionic complexes

e.g. $Fe(H_2O)_6^{2+}$, $[Co(NH_3)_4Cl_2]^+$





- Many coordination compounds are colored
- Many coordination compounds are paramagnetic

Oxidation States

- See Table 20.2 for common oxidation states of the 1st-row transition metals

- +1 up to +7 are observed, with +2 and +3 most common

- As the oxidation state is increased, the d orbitals are stabilized, and the metals get harder to oxidize further

- Ionization energies go up from left to right- follows trend in effective nuclear charge

Ionization energies

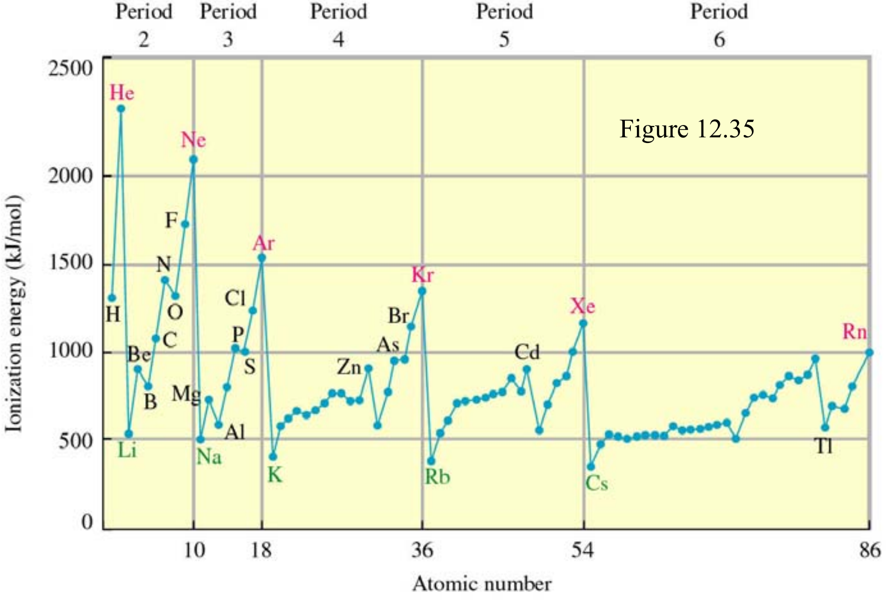
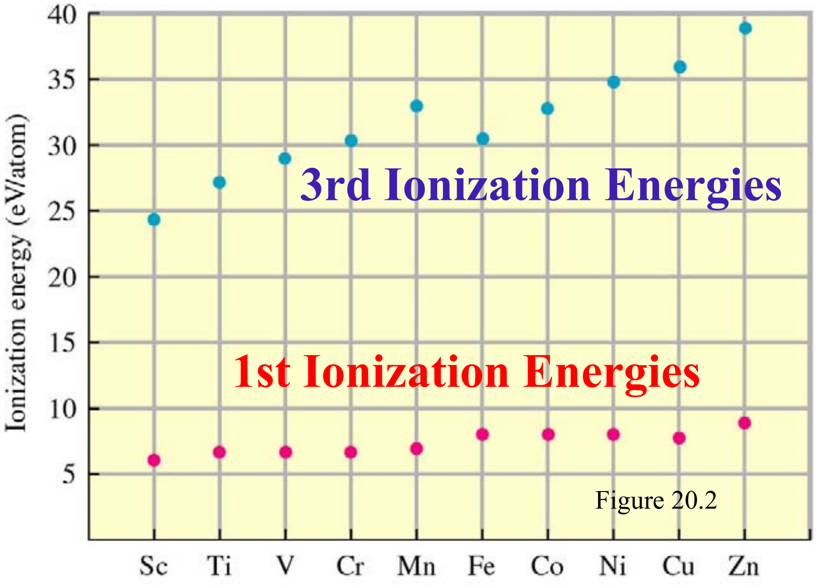


Figure 12.35

Ionization energies



3rd Ionization Energies

1st Ionization Energies

Figure 20.2

Standard Reduction Potentials

- Consider the reduction half-reaction:

$$M \longrightarrow M^{n+} + ne^-$$

Table 20.3 lists reduction potentials (ε°) for 1st-row transition metals in aqueous solutions:

Ti --> Ti^{2+} + $2e^-$	1.63V
V --> V^{2+} + $2e^-$	1.2V
Mn --> Mn^{2+} + $2e^-$	1.18V
Cr --> Cr^{2+} + $2e^-$	0.91V
Zn --> Zn^{2+} + $2e^-$	0.76V
Fe --> Fe^{2+} + $2e^-$	0.44V
Co --> Co^{2+} + $2e^-$	0.28V
Ni --> Ni^{2+} + $2e^-$	0.23V
Cu --> Cu^{2+} + $2e^-$	-0.34V

↑ reducing ability

Since ε° is defined by the process

$$2H^+ + 2e^- \longrightarrow H_2$$

all of the metals except Cu can reduce H^+ to H_2 in concentrated aqueous acids.

Atomic radii

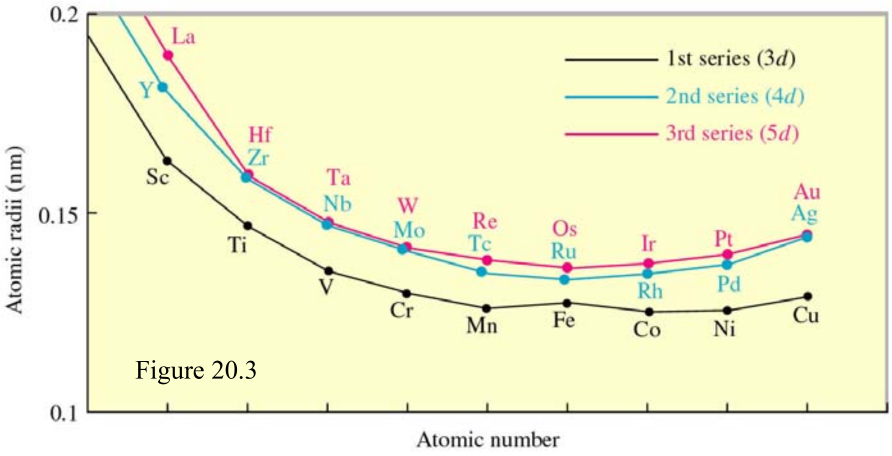


Figure 20.3

Lanthanide Contraction

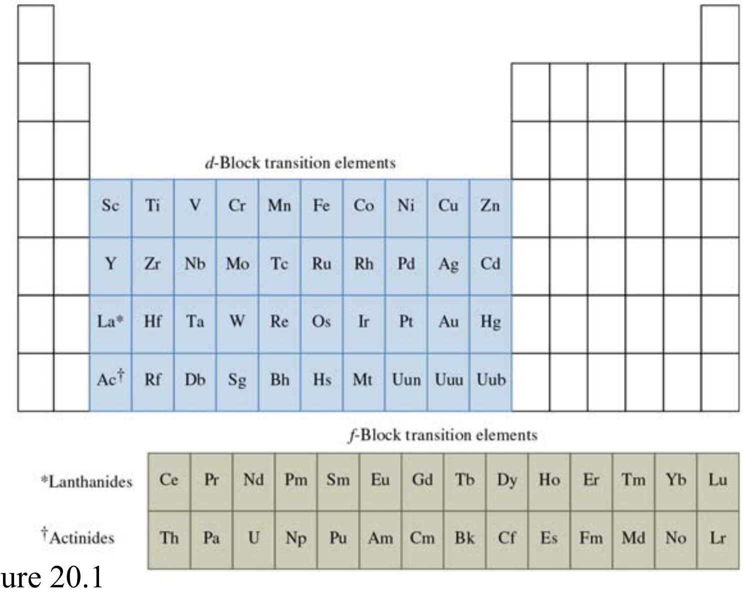


Figure 20.1

Titanium (0.6% by mass of Earth's crust)

- Titanium metal- characterized by low density, high strength, chemical inertness- used as a structural element in high-demand uses such as jet engines, high-performance bicycles, etc.

- Titanium ions- often found in +4 oxidation state (indicated as Ti^{4+}, or Ti(IV))

$$TiCl_4(l) + 2H_2O(l) \longrightarrow TiO_2(s) + HCl(g)$$

- In the +3 oxidation state, Titanium in Sapphire ($Ti^{3+}:Al_2O_3$) is one of the most important commercial laser materials

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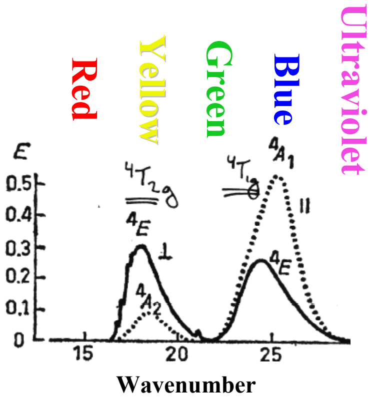
Vanadium (V)- (Scandinavian goddess, *Vanadis*)

- Named after the Scandinavian goddess because of its beautiful multicolored compounds!
- About 80% of the vanadium now produced is used as a steel additive
- Most common oxidation state is +5, as in V_2O_5. This oxide is a widely used redox catalyst

Chromium (Cr)- (greek *chroma*, color)

- Cr(0) (metal) is used for making steel. Cr(VI) and Cr(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving.
- Chromium enters the air, water, and soil mostly as Cr(III) and Cr(VI). Cr(III) strongly attaches to soil, but a small amount can dissolve in water and move deeper to underground water reservoirs - pollutant from Erin Brockovich.

The colors of many gemstones come from Cr^{3+} impurities



Ruby: Cr^{3+} in Al_2O_3

Manganese (Mn)

(Latin *magnes*, magnet, from magnetic properties of pyrolusite, MnO_2)

- Manganese minerals are widely distributed, primarily as oxides, silicates, and carbonates.
- Mn is the only transition metal that can exist in all oxidations states from +2 to +7
- A manganese catalyst in green plants is responsible for all of the oxygen in our environment, produced through photosynthesis.
- Mn is used to form many important alloys. In steel, Mn improves the rolling and forging qualities, strength, toughness, stiffness, and other properties.

Iron (Fe)

- The use of iron is prehistoric. Many important alloys are primarily iron, including alloys with carbon, Mn, Ni, Cr, etc.
- High abundance in the universe- found in the sun and many stars in considerable quantity. Iron is a principal component of one class of meteorites, the *siderites*.
- The core of the earth is thought to be ca. 90% iron. The most common iron ore in the Earth's crust is *hematite* (Fe_2O_3)
- Fe is a vital element for plant and animal life. For example, it is at the core of hemoglobin, the oxygen transporter in our blood.
- Iron is the cheapest, most abundant, useful, and important of all metals.

Cobalt (Co)

(German *Kobald*, goblin or evil spirit. Greek *cobalos*, mine)

- Occurs in many minerals, often associated with Ni, Ag, Pb, Cu, and Fe ores
- Important metal for magnetic applications, including magnetic steels and magnetic shielding alloys.
- Cobalt salts have been used for centuries as color pigments (cobalt blues) in porcelain, glass, pottery, and enamels

Nickel (Ni)

(German, from *kupfernickel*, "Old Nick's copper" or Satan's copper)

- As a metal, it is chiefly valued for its alloys with Fe and Co
- Fine Ni powders used as catalysts for hydrogenation reactions

Copper (Cu)

(Latin *cuprum*, from the island of cyprus)

- Said to have been mined for > 5000 years
- Cu metal is highly conductive of heat and electricity
- Most important copper ores are sulfides, oxides, and carbonates

Zinc (Zn)

(German *Zink*, of obscure origin)

- Centuries before it was recognized as a distinct element, Zn ores were used for making brass
- ZnO is widely used in the manufacture of paints, cosmetics, pastics, storage batteries, and electrical equipment among others.
- ZnS (among the most abundant natural ores of Zn) is used as an important phosphor material in X-ray and TV screens, and in fluorescent lights

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Chapter 20: Transition Metals and Coordination Chemistry

20.1 Survey of transition metals

20.2 1st-row transition metals

Read section 20.2 and Tables 20.4 - 20.11 for further general descriptions of the 1st row transition metals and their uses.

→ 20.3 Coordination compounds

→ 20.4 Isomerism

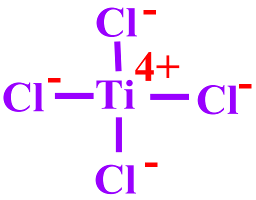
20.5 Bonding in complex ions: The localized electron model

20.6 The crystal field model

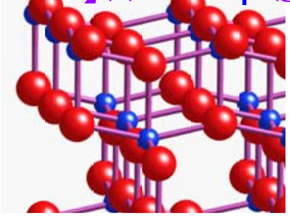
20.7 The molecular orbital model

20.8 The biological importance of coordination complexes

$TiCl_4(l) + 2H_2O(l) \longrightarrow TiO_2(s) + HCl(g)$



coordination compound

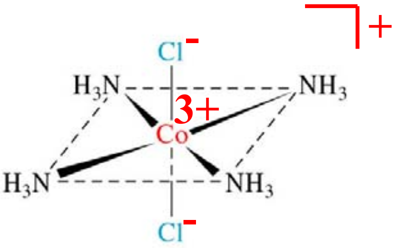


semiconductor (network solid)

In $TiCl_4$:

- Coordination number = 4
- Cl^- is the "Ligand"
- Overall charge neutral

$[Co(NH_3)_4Cl_2]^+$



Coordination number = 6

- Cl^- and NH_3 are the ligands
- Overall charge = +1

- This complex is charged and so must have a counter ion, e.g. $[Co(NH_3)_4Cl_2]Cl$
- This complex will ionize in solution-> electrolyte

The Nobel Prize in Chemistry 1913

Alfred Werner (University of Zurich, Switzerland)
"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry"

Prior to Werner's work, it was not known how the atoms in a molecule of the chemical formula $[Pt(NH_3)_2Cl_2]$ were connected. The theories at the time predicted such molecules to be connected as linear chains: $[Pt\text{-}NH_3\text{-}NH_3\text{-}Cl]Cl$ or $Cl\text{-}NH_3\text{-}Pt\text{-}NH_3\text{-}Cl$

Werner studied the conductivities of solutions. Other factors being equal, the conductivity of an aqueous solution of an ionic salt is proportional to the number of ions produced when the salt is dissolved.

Werner studied the following series:

$[Pt(NH_3)_6]Cl_4$ has relatively high conductivity (more ions)
$[Pt(NH_3)_5Cl]Cl_3$ has decreasing conductivity
$[Pt(NH_3)_4Cl_2]Cl_2$ has decreasing conductivity
$[Pt(NH_3)_3Cl_3]Cl$ has decreasing conductivity
$[Pt(NH_3)_2Cl_4]$ has zero conductivity
$K[Pt(NH_3)Cl_5]$ has increasing conductivity
$K_2[PtCl_6]$ has increasing conductivity

These experiments led Werner to postulate the presence of 2 different types of bonding in inorganic coordination compounds:

1. **Primary valences**, fixed in number by charge balance; these were ionic (i.e. to ions only) and non-directional.
2. **Secondary valences**, determined by the nature of the central metal atom (usually 4 or 6); non-ionic, directional.

- An important study of Werner's was of $[Pt(NH_3)_2Cl_2]$.
- 2 compounds having this same chemical formula but different properties were known. According to the theory of the day, these two were the structures:

  $[Pt\text{-}NH_3\text{-}NH_3\text{-}Cl]Cl$, in which one chloride should be ionic

  $Pt(\text{-}NH_3Cl)_2$, in which neither chloride should be ionic

- Werner found no ionic chlorides in either, and suggested the following structures instead:

- Two compounds having the same chemical formula but different structures are called *isomers*.
- These experiments changed our understanding of bonding to transition metal ions- coordination complexes are sometimes still referred to as Werner complexes

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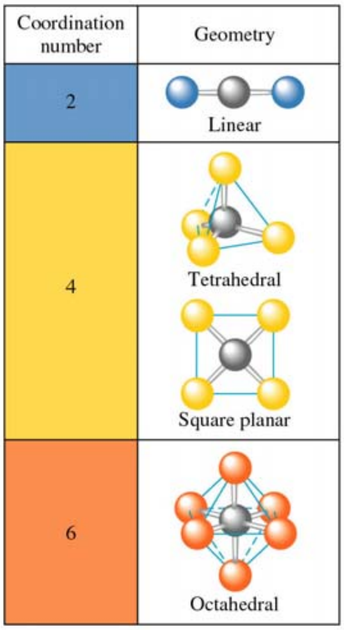
Many metal ions can form complexes of more than one coordination number

Some limiting geometries:



Coordination number	Geometry
2	Linear
4	Tetrahedral Square planar
6	Octahedral

Figure 20.6

Ligands

- The *ligand* is the molecule, atom, or ion bound to a central metal atom.
- Transition metal ions are Lewis acids (they are electron poor, and wish to accept electrons)
- Ligands are therefore electron donors, or Lewis bases.
- Some common ligands: Cl^-, NH_3, H_2O

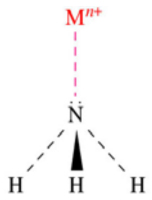


Figure 20.7

Types of Ligands

- Depending on the number of electron lone pairs available, ligands will bond to a metal through 1 (*monodentate*), 2 (*bidentate*), 3 (*tridentate*), ... atoms
- Any polydentate ligand is also called a *chelating* ligand
- Cl^-, NH_3, H_2O are all monodentate ligands
- Ethylenediamine (en) is a common bidentate ligand

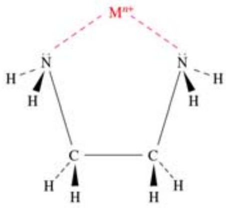


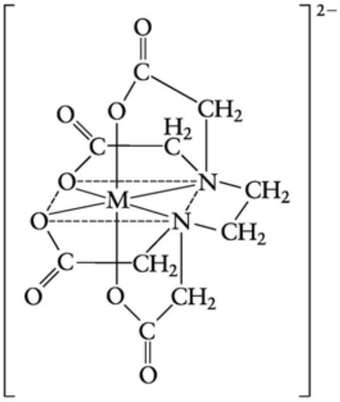
Figure 20.7

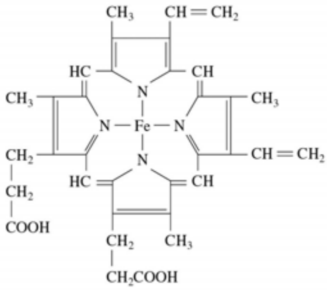
- **Some polydentate ligands:**

Ethylenediaminetetraacetate (EDTA)

a common hexadentate ligand

Figure 20.8





Porphyrin

a common class of tetradentate ligands found in biology (e.g. hemoglobin)