

Chapter 22

The Transition Metals

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22.2c Stability and the Chelate Effect

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cis-trans

fac-mer

optical—don't do this, I think

22.3 Coordination Compounds: Bonding and Spectroscopy

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Donor-Acceptor Interactions

Octahedral Sigma-Only MOs

Octahedral Pi Donor and Acceptor Ligands

Other Geometries

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d-d Spectrochemical Series

High-Spin/Low-Spin

Cases:

Why is $\text{Cu}(\text{NH}_3)_6^{2+}$ more darkly colored than $\text{Cu}(\text{H}_2\text{O})_6^{2+}$?

Why is $\text{Mn}^{2+}(\text{aq})$ colorless?

Why is $\text{Co}(\text{CO})_6$ colorless?

Why is Zn^{2+} colorless?

What makes MnO_4^- deeply colored?

22.4 Coordination Compounds: Reactivity

22.4a Substitution Reactions

22.4b Oxidation-Reduction Reactions

22.4c Reactions of Bonded Ligands

(NOTE: I don't know where to put common oxidation states and have put the tables at the end-by)

In This Chapter...

We have used our understanding of basic principles of chemistry to undertake brief explorations of the properties and reactivity of organic compounds and main group elements, particularly those of the p-block elements. We now turn to the more complex chemistry of the d-block transition metals and the f-block lanthanides and actinides. Although these elements are less pervasive in our lives and less famous, as elements go, they play crucial roles in the manufacture of modern materials and in many important biological processes. Much of our exploration here will center on the d-block transition metals and we will examine how the metals are formed from their ores, used in alloys, and used to form coordination complexes, which are special types of Lewis acid-base compounds.

3B	4B	5B	6B	7B	8B		1B	2B	
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	Rf	Db	Sg	Bh	Hs	Mt			

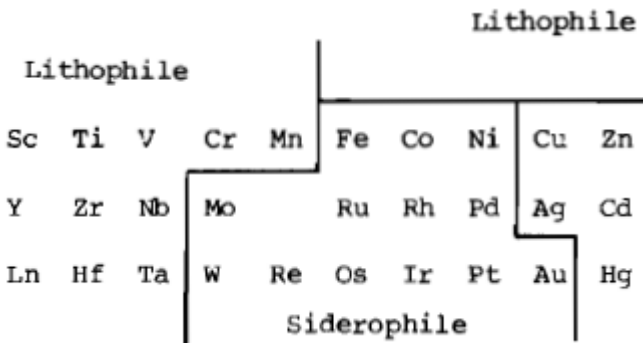
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22.1 Properties and Occurrence of Transition Metals

Metals, as you know, tend to form cations in their chemical compounds. They are generally more stable in their cationic form as a part of a compound than as neutral elemental metals. As such

Interactive Simulation/Exercise: Electronegativity and Common Ore Types (new to be made)

Maybe video of Charlie at the giant Copper Mine



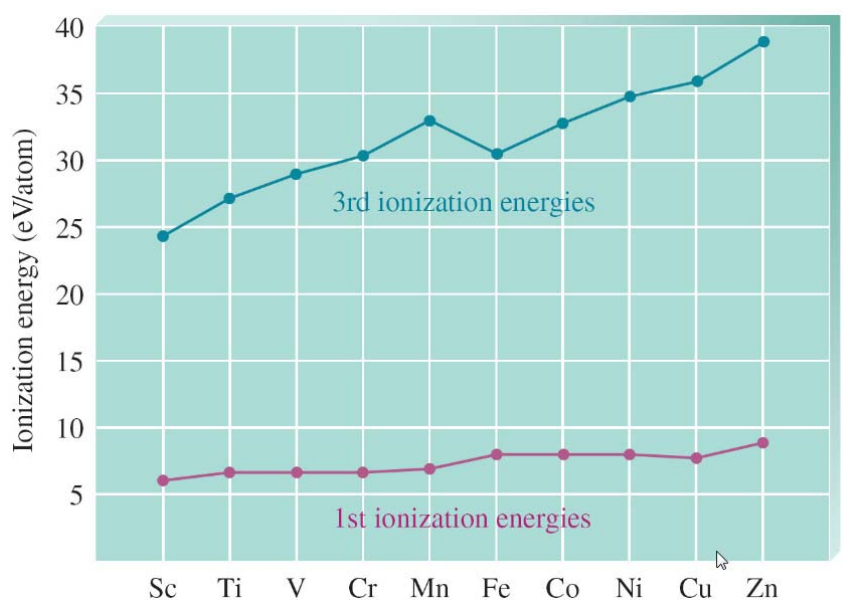
get geochemistry text pg. 107

22.1a Periodic Trends Among the d-Block Elements

In Chapter 7 we analyzed the periodic properties of the elements and centered our analysis on the main group elements. We found that in general atoms have smaller, lower energy valence orbitals in the top right region of the periodic table, and larger, higher energy orbitals in the lower left of the table. This central trend predicted many of the trends in atomic properties we observed.

Ionization Energy

For example, ionization energy (the energy needed to remove an electron from a free atom) generally increases moving left-to-right across the periodic table because of increasing effective nuclear charge, and decreases moving down a group because of higher principal quantum number. Figure 22.XXX shows the first and third ionization ($M^{2+} \rightarrow M^{3+}$) energies of the first row of transition metals.



s vs. d orbital loss

Counter to expectations, the 1st ionization energy hardly changes at all. However, the 3rd ionization energy does display the expected increase. How is this explained? We need to consider the electron configurations of the atoms and ions involved. Each transition metal contains at least 1 4s electron and one or more 3d electrons. While the 4s orbital “fills” before the 3d orbitals, recall that when a cation is formed, the 4s electrons are lost first. That means the first IE for each atom is the result of losing a 4s electron. Starting with Sc and moving left-to-right across the periodic table, each move to the right leads to a +1 increase in the nuclear charge and the addition of 1 electron to the 3d subshell. Because they are in a lower n shell, the 3d electrons are good at shielding the 4s electrons. That means the effective nuclear charge experienced by the 4s electrons does not increase moving across the transition series. And, therefore, neither does the ionization energies of those elements.

The 3rd ionization is a measure of removing a 3d electron, after any 4s electrons have been removed. In this case the anticipated result of increasing Z^* moving left-to-right is observed.

(This all needs images showing electron configuration diagrams and what happens in each of these steps for representative examples.)

Electronegativity

Electronegativity continues the trend of minimal changes moving across the transition metal series. Consider moving left-to-right six elements from Li to F with that of moving six elements from Sc to Co. In the case of the main group elements, electronegativity changes from nearly the smallest (Li = 1.0) to the highest (F = 4.0). In the transition series the change is small (Sc = 1.3 to Co = 1.7).

■ **Table 5-3** Electronegativity Values of the Elements^a

1A												3A 4A 5A 6A 7A					8A										
1	H 2.1											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	He										
2	Li 1.0	Be 1.5											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ne									
3	Na 1.0	Mg 1.2	3B		4B	5B	6B	7B	8B			1B	2B	Ga 1.5	Ge 1.9	As 2.1	Se 2.4	Br 2.8	Kr								
4	K 0.9	Ca 1.0	Sc 1.3	Ti 1.4	V 1.5	Cr 1.6	Mn 1.6	Fe 1.7	Co 1.7	Ni 1.8	Cu 1.8	Zn 1.6	Ga 1.7	Ge 1.9	As 2.1	Se 2.4	Br 2.8	Kr									
5	Rb 0.9	Sr 1.0	Y 1.2	Zr 1.3	Nb 1.5	Mo 1.6	Tc 1.7	Ru 1.8	Rh 1.8	Pd 1.8	Ag 1.6	Cd 1.6	In 1.6	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe									
6	Cs 0.8	Ba 1.0	La 1.1	Hf 1.3	Ta 1.4	W 1.5	Re 1.7	Os 1.9	Ir 1.9	Pt 1.8	Au 1.9	Hg 1.7	Tl 1.6	Pb 1.7	Bi 1.8	Po 1.9	At 2.1	Rn									
7	Fr 0.8	Ra 1.0	Ac 1.1																								
			* Ce 1.1												Pr 1.1	Nd 1.1	Pm 1.1	Sm 1.1	Eu 1.1	Gd 1.1	Tb 1.1	Dy 1.1	Ho 1.1	Er 1.1	Tm 1.1	Yb 1.0	Lu 1.2
			† Th 1.2												Pa 1.3	U 1.5	Np 1.3	Pu 1.3	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.5

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22.1b Common Ores of the Transition Metals

Almost all metals are found in nature as part of compounds, along with anionic species. A rock body rich in a particular elements is an “ore” of that element. However, the particular ore form each element prefers varies as a function of it position on the periodic table. The metallic character of an element is a measure of how metallic an element acts. In one sense of this definition, it is a marker of the tendency of a metallic element to form ionic bonds as opposed to covalent bonds when bonding with a nonmetal. Elements of greater metallic character tend to form stable oxide compounds; those with lesser metallic character form sulfide ores, or even exist in the elemental (native) state in nature.

Metals are classified in terms of what kinds of ores they form. Those transition elements on the far left tend to form oxide ores. These are called lithophile elements. Those on the right side are called chalcophiles, and form sulfide ores. Some, toward the lower right, do sometimes exist as the native, neutral metal. These trends are a result of the elements tendency to form ionic vs. covalent bonds, and as such are a result of the element’s electronegativity.

lithophile: Sc, Ti, V, Cr, Mn, (Fe)

Y, Zr, Nb

La, Hf, Ta, W

Siderophile: Fe, Co, Ni
 Mo, Ru, Rh, Pd
 (W), Re, Os, Ir, Pt, Au

Chalcophile: (Fe), Cu, Zn
 (Mo), Ag, Cd
 Hg

Some common ores of the transition metals are shown in Table 22.1 (*data for tables on the next few pages*)

■ **Table 22-1** Common Classes of Ores

Anion	Examples and Names of Minerals
none (native ores)	Au, Ag, Pt, Os, Ir, Ru, Rh, Pd, As, Sb, Bi, Cu
oxide	hematite, Fe_2O_3 ; magnetite, Fe_3O_4 ; bauxite, Al_2O_3 ; cassiterite, SnO_2 ; periclase, MgO ; silica, SiO_2
sulfide	chalcopyrite, CuFeS_2 ; chalcocite, Cu_2S ; sphalerite, ZnS ; galena, PbS ; iron pyrites, FeS_2 ; cinnabar, HgS
chloride	rock salt, NaCl ; sylvite, KCl ; carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
carbonate	limestone, CaCO_3 ; magnesite, MgCO_3 ; dolomite, $\text{MgCO}_3 \cdot \text{CaCO}_3$; rhodochrosite, MnCO_3
sulfate	gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; epsom salts, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; barite, BaSO_4
silicate	beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$; kaolinite, $\text{Al}_2(\text{Si}_2\text{O}_6)(\text{OH})_4$; spodumene, $\text{LiAl}(\text{SiO}_3)_2$

TABLE 3.13 Principal Ores of the Technologically Important Metals

The Abundant Metals

Principal Ores	Metal	Principal Ores
Magnetite, Fe_3O_4 ; hematite, Fe_2O_3 ; goethite, $HFeO_2$ siderite, $FeCO_3$	Titanium	Ilmenite, $FeTiO_3$; rutile, TiO_2
Gibbsite, H_3AlO_3 ; diaspore, $HALO_2$; boehmite, $HALO_2$; kaolinite, $Al_4Si_4O_{10}(OH)_8$	Manganese	Pyrolusite, MnO_2 ; psilomelane, $BaMn_9O_{18} \cdot 2H_2O$ cryptomelane, KMn_8O_{16} ; rhodocrosite, $MnCO_3$
	Magnesium	Magnesite, $MgCO_3$; dolomite, $CaMg(CO_3)_2$

The Scarce Metals

forming sulfide minerals (Chalcopile)

Principal Ores	Metal	Principle Ores
Covellite, CuS , chalcocite, Cu_2S ; digenite, Cu_9S_5	Cadmium	Substitution for Zn in sphalerite
chalcopyrite, $CuFeS_2$; bornite, Cu_5FeS_4 ; tetrahedrite, $Cu_{12}Sb_4S_{13}$	Cobalt	Linnaeite, Co_3S_4 ; substitution for Fe in pyrite, FeS_2 ;
Sphalerite, ZnS	Mercury	Cinnabar, HgS ; metacinnabar, HgS
Galena, PbS	Silver	Acanthite, Ag_2S ; substitution for Cu and Pb in their common ore minerals
Pentlandite $(NiFe)_9S_8$; garnierite, $H_4Ni_3Si_2O_9$	Bismuth	Bismuthinite, Bi_2S_3
Stibnite, Sb_2S_3		
Molybdenite, MoS_2		
Arsenopyrite, $FeAsS$; orpiment, As_2S_3 ; realgar, AsS		

... found in the native form (Siderophile)

Principle Ores	Metal	Principle Ores
Calaverite, AuTe ₂ ; krennerite, (Au,Ag)Te ₂ ; nylvante, AuAgTe ₄ ; petzite, AuAg ₃ Te ₂	Palladium	Arsenopalladinite, Pd ₃ As; michenerite, PdBi ₂ ; frodite, PdBi ₂
	Rhodium	-
Sperryllite, PtAs ₂ ; braggite, PtS ₂ ; cooperite, PtS	Iridium	-
	Ruthenium	Laurite, RuS ₂
	Osmium	-

TABLE 3.13 Principal Ores of the Technologically
Important Metals

The Scarce Metals

Commonly associated with oxygen (Lithophile)

Metal	Principal Ores	Metal	Principal Ores
Chromium	Chromite, Fe ₂ CrO ₄	Niobium and Tantalum	Columbite, FeNb ₂ O ₆ ; pyrochlore, NaCaNb ₂ O ₆ F; tantalite, FeTa ₂ O ₆
Tin	Cassiterite, SnO ₂	Thorium	Monazite, a rare-earth phosphate containing thorium by atomic substitution
Tungsten	Wolframite, FeWO ₄ ; scheelite, CaWO ₄	Beryllium	Beryl, Be ₃ Al ₂ (SiO ₃) ₆
Uranium	Uraninite (pitchblende), UO ₂ ; carnotite, K ₂ (UO ₂) ₂ (VO ₄) ₂ ·3H ₂ O; substituting for Fe in magnetite, Fe ₃ O ₄		

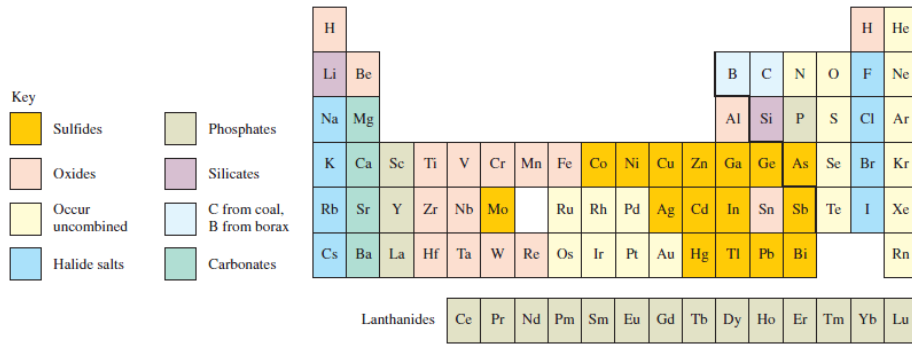
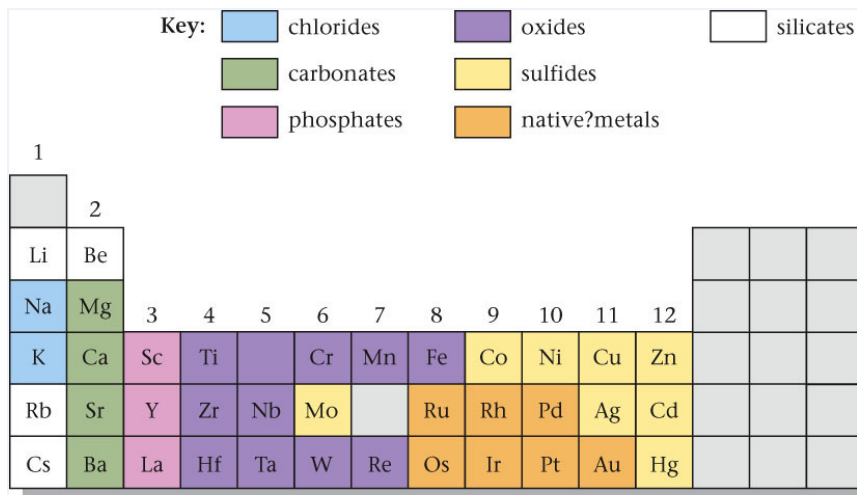


Figure 22-1 Major natural sources of the elements. The soluble halide salts are found in oceans, salt lakes, brine wells, and solid deposits. Most helium is obtained from wells in the United States and Russia. Most of the other noble gases are obtained from air.

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masterton 2002

Table 21.19 ▶ Common Minerals Found in Ores

Anion	Examples
None (free metal)	Au, Ag, Pt, Pd, Rh, Ir, Ru
Oxide	Fe ₂ O ₃ (hematite) Fe ₃ O ₄ (magnetite) Al ₂ O ₃ (bauxite) SnO ₂ (cassiterite)
Sulfide	PbS (galena) ZnS (sphalerite) FeS ₂ (pyrite) HgS (cinnabar) Cu ₂ S (chalcocite)
Chloride	NaCl (rock salt) KCl (sylvite) KCl · MgCl ₂ (carnalite)
Carbonate	FeCO ₃ (siderite) CaCO ₃ (limestone) MgCO ₃ (magnesite) MgCO ₃ · CaCO ₃ (dolomite)
Sulfate	CaSO ₄ · 2H ₂ O (gypsum) BaSO ₄ (barite)
Silicate	Be ₃ Al ₂ Si ₆ O ₁₈ (beryl) Al ₂ (Si ₂ O ₈)(OH) ₄ (kaolinite) LiAl(SiO ₃) ₂ (spodumene)

zum Dahl—rework completely,

22.1c Extraction of Metals from Ores

Most metals exist as positively charged ions in ionic compounds. The process of chemically reacting the ore to give the neutral metal is called *extraction*. Because the metal is positively charged in the ore, the extraction requires reduction of the metal cation to the neutral state. The process used for reducing the metal depends on the difficulty of reduction. Figure 22.XXX shows different metals as a function of how difficult it is to reduce the cation to the neutral metal.

■ **Table 22-2** Reduction Processes for Some Metals

Metal Ion	Typical Reduction Process
lithium, Li ⁺ potassium, K ⁺ calcium, Ca ²⁺ sodium, Na ⁺ magnesium, Mg ²⁺ aluminum, Al ³⁺	Electrolysis of molten salt
manganese, Mn ²⁺ zinc, Zn ²⁺ chromium, Cr ²⁺ , Cr ³⁺ iron, Fe ²⁺ , Fe ³⁺	Reaction of oxide with coke (carbon) or carbon monoxide (CO)
lead, Pb ²⁺ copper, Cu ²⁺ silver, Ag ⁺ mercury, Hg ²⁺ platinum, Pt ²⁺ gold, Au ⁺	Element occurring free, or easily obtained by roasting the sulfide or oxide ore

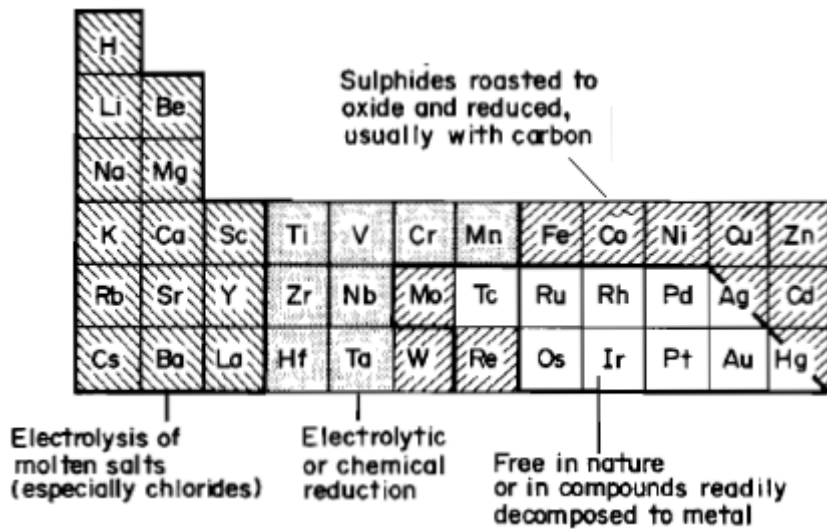
Increasing activity of metals

whitten 846: Make something like the above, but with the data below; the arrow says "Difficulty of Reduction"

Most difficult to reduce	$\text{Na}^+, \text{Al}^{3+}, \text{Ti}^{4+}$	Electrolysis or Reaction with a metal formed by electrolysis
Moderately difficult to reduce	$\text{Fe}^{3+}, \text{Ni}^{2+}, \text{Cu}^{2+}$	Reduction of oxide with Carbon; Sometimes preceded by "roasting" of sulfide ore to form oxide
Easy to Reduce	Hg^{2+}	Simple heating of oxide or reaction of sulfide with O_2
Element found in Metallic Form	Au, Pt, Pd	Leaching of metal from surrounding rock

Very difficult to reduce metals such as sodium and aluminum are reduced electrolytically. Most main group metals (Li, Na, K, Mg, Ca, Al) are produced by electrolytic reduction, or by chemical reduction using a metal that was formed electrolytically. Transition metals tend to be more easily reduced and are formed from the ore by reaction with coke, which is mainly elemental carbon. Toward the right side of the transition metal block, many elements are particularly easy to reduce and can be formed from the ore by simple heating. An example of this is mercury, which can be formed by "roasting" its sulfide ore.

Figure 22.XXX shows the primary method or methods used for extracting different metallic elements.



Notice the trend from left-to-right across the periodic table, where elements to the left are produced via reduction by electrolysis, those in the middle and towards the top are formed via reduction with carbon.

Those in the lower left are found free in nature, or can be formed by simple heating. This follows the periodic trends discussed for electronegativity: elements on the left are least electronegative, are the most difficult to reduce from the cationic to the metallic state, and require electrolytic reduction. Those on the lower right are most electronegative, easiest to reduce, and are often found in nature in the neutral metallic state. Those in the middle require the more moderate carbon reduction process.

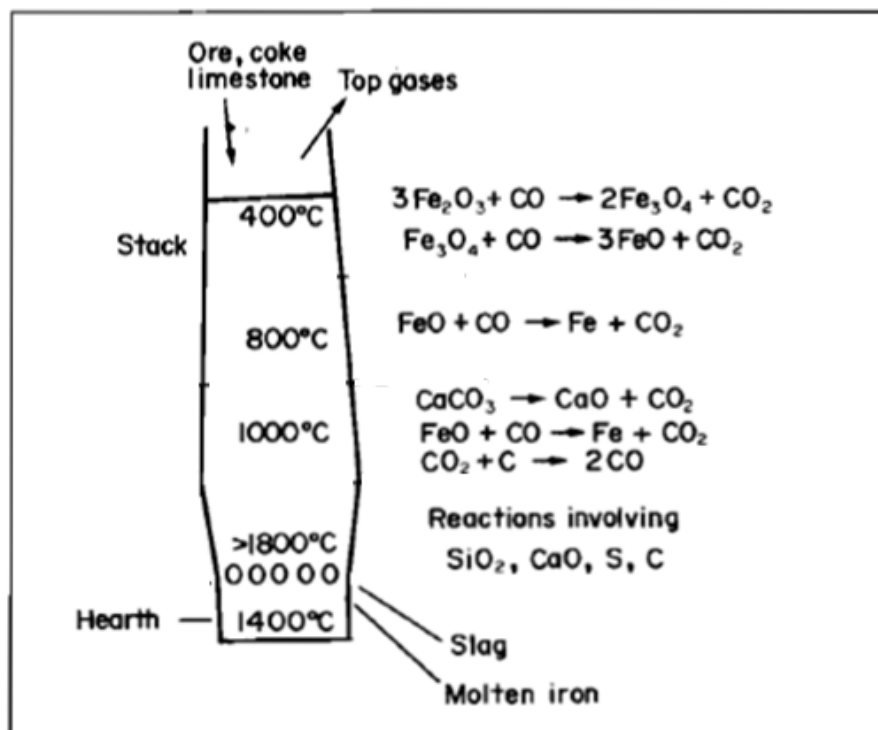
We show how four representative metals are obtained from their ores here.

Iron

Iron is found in a large variety of ores, both as an oxide and as a sulfide. Iron sulfides are treated prior to reduction by reaction with oxygen to convert the sulfide to an oxide.

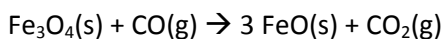
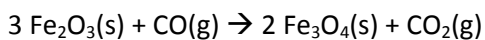
reaction here:

Iron (III) oxide is reduced to the metal by reaction with carbon in a "blast furnace." The reactions that take place are outlined in Figure 22.XXX. The iron(III) oxide is reduced in a series of steps.

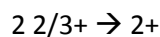
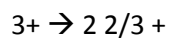


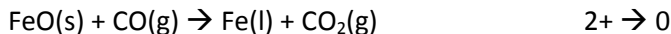
zumdahl 8e pg 991 is good as a start

Reaction:



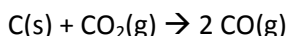
Fe Oxidation State Change:





Notice that in each step the oxidation state of the carbon (in CO) increases by 2, from +2 to +4. But also notice that while the reactant added to the blast furnace is C(s), the reactant involved in the reduction reactions is always CO(g). Why is this? The reason is that two solids react together very slowly because they can only react where their surfaces come in contact. This is difficult for two solids. The reaction between a solid and a gas (in this case CO) is much more kinetically favored because the gas can envelope all available surface area of the solid, even inside pores and cracks.

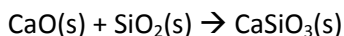
The CO is produced via the reaction of CO₂ and C,



which is favored above XXX °C. In order for enough CO₂ to be available to react with the added C(s), CaCO₃ is also added as a reactant. It undergoes decomposition at high temperatures,



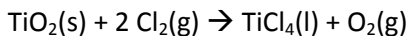
The product CaO serves an additional important role in removing silicate impurities, which are invariably present in large-scale operations involving native rock.



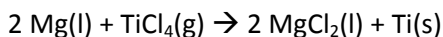
This product is part of the waste stream called "slag."

Titanium

Titanium forms difficult to reduce cationic species, too difficult to reduce using carbon as is done for iron. Because of this difficulty, the neutral metal is produced by chemical reduction using electrolytically produced Mg metal at high temperatures. One principal ore of titanium is rutile, TiO₂. The first step to form metallic titanium is to convert TiO₂ into TiCl₄.

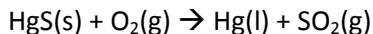


Although this reaction does not reduce the titanium, which remains in the +4 oxidation state, it does form the more reactive chloride that is used in the reduction step.



Mercury

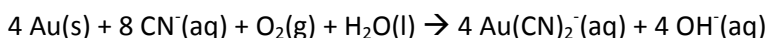
The principal ore of mercury is cinnabar, HgS. Because the Hg²⁺ cation is easily reduced, cinnabar reacts readily with oxygen when heated,



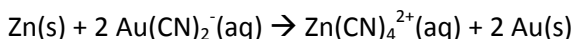
Because this reaction is so simple, metallic mercury was one of the first known metals in ancient times.

Gold

Some ores, most importantly those of gold, contain the native metallic element. In these cases the chore is to separate the gold from the rest of the rock. The difficulty is that the gold is very dilute- often as little as 25 parts per million- so a tiny amount of gold must be separated from a large amount of rock. The method most used today is to chemically react the gold with cyanide ion to dissolve and “leach” it from the rest of the rock, which is crushed into a powder before treating. The dissolution reaction is,



Once free of the insoluble rock, metallic gold can be reformed by reduction. This is often done using zinc metal,



The gold-depleted rock is disposed of on site in piles called “tailings.”

22.2 Coordination Compounds: Structure and Isomerism

Section Introduction

Transition metal coordination complexes are Lewis acid-base adducts where a single Lewis acid- a metal cation- bonds with multiple Lewis bases- the ligands. A large branch of chemistry involves synthesizing compounds with just the right set of ligands around just the right metal ion, in just the right spatial arrangement to lead to a compound with particularly desired properties. This section introduces the structural aspects of these compounds.

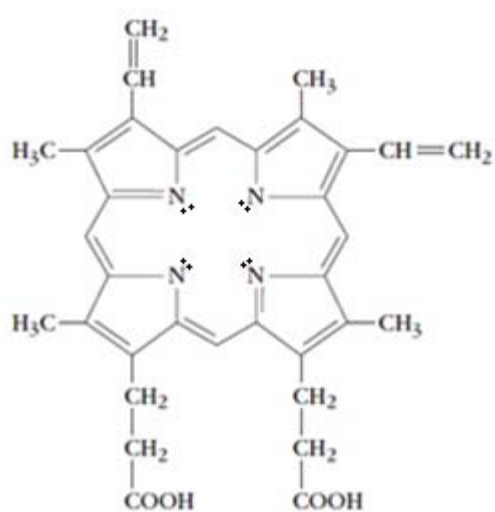
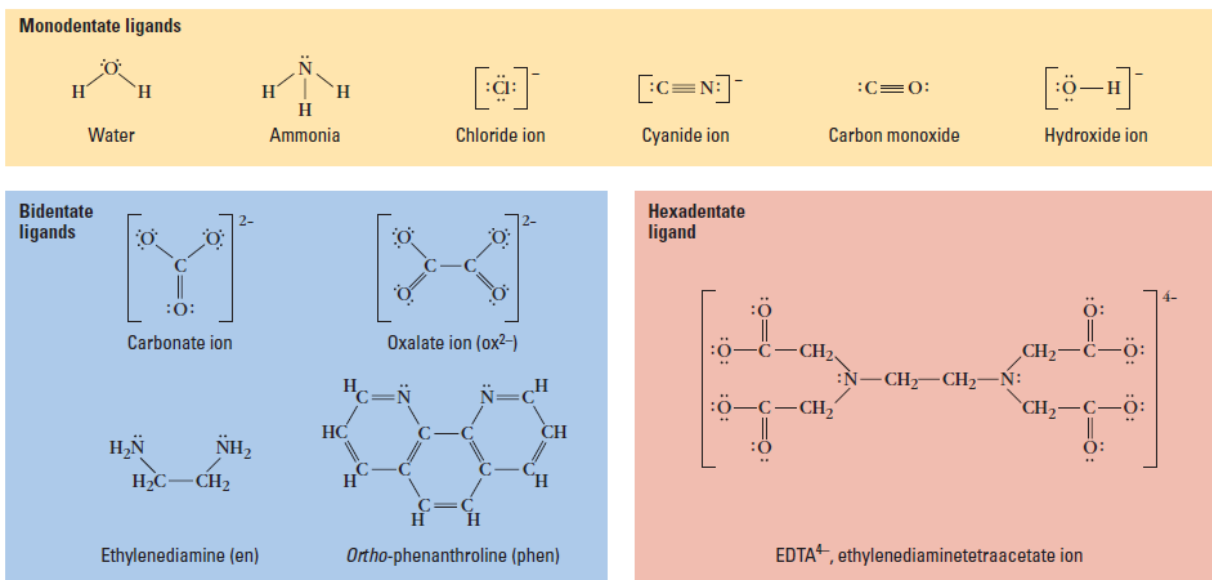
Interactive module will be a walk-through of the anatomy of a transition metal complex. It will include a simple animation of separate ligands moving in to bond to the metal.

22.2a Ligands, Denticity, and Coordination Number

When a coordination compound forms, a central metal ion acts as a Lewis acid and forms multiple coordinate covalent bonds to ligands, which act as Lewis bases. (The term ligand is also used in biology

but is pronounced differently. In inorganic chemistry a soft “i” is used, as in “lignin”; in biology a hard “l” is used, as in “lion.”)

Some typical ligands are shown in Figure 22.XXX.



Heme



dien



trien

Moore 22.9; add PPh₃, dien, and trien (note them as tri and tetradentate), add heme, remove Carbonate

Some definitions:

Central Metal: The metal atom or ion at the center of the coordination compound.

Coordination Number: The number of atoms to which a central metal is bonded.

Ligand Denticity: The number of attachments to the metal a single ligand has. Bidentate = two attachments, tridentate = three attachments, ect.

Chelate: A ligand that has 2 or more attachments to the central metal.

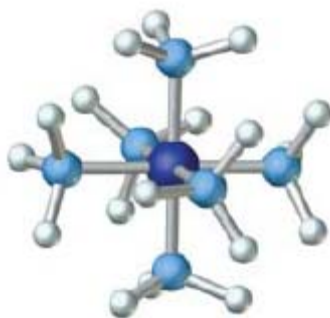
Inner Coordination Sphere: Those ligands directly bonded to the central metal.

Counter Ion: An ion present as part of a salt to balance the charge of the metal-containing complex ion, but not bonded to the central metal atom.

Outer Coordination Sphere: Any counterions or waters of hydration associated with the metal complex, but not directly bonded to the central metal.

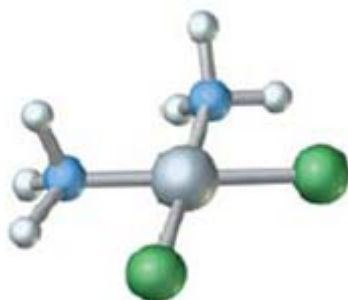
Examples

Coordination Number



Octahedral
 $[\text{Co}(\text{NH}_3)_6]^{3+}$

6-coordinate



4-coordinate

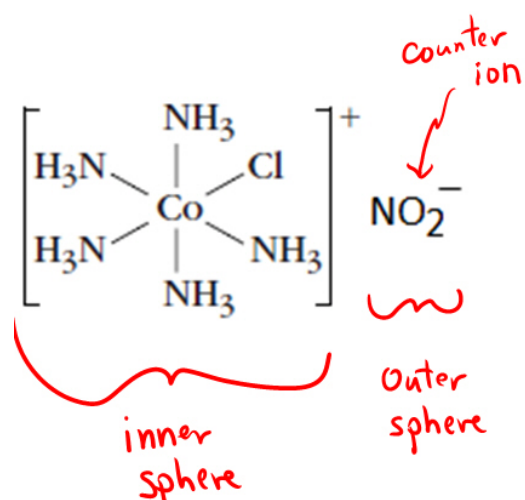
Ligand Denticity

Ligands are classified by the number of attachments they form to a central metal atom.

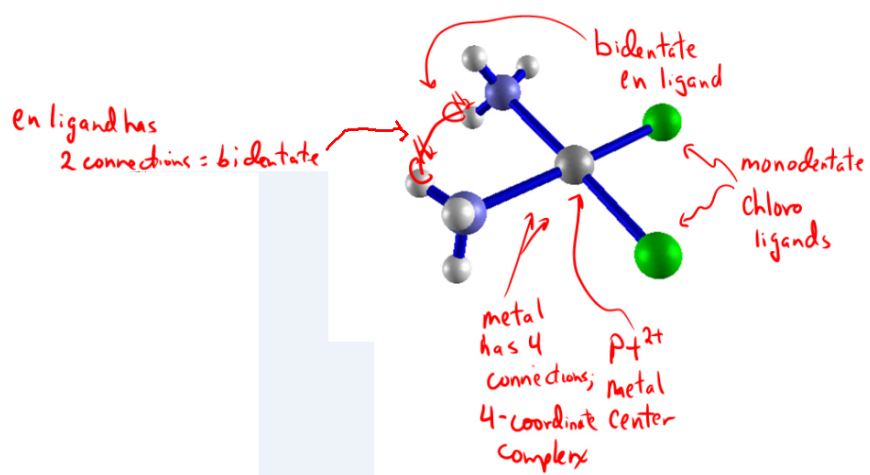
<u>attachments</u>	<u>classification</u>	<u>example</u>
1	monodentate	NH_3 , H_2O , Cl^-
2	bidentate	en, $\text{C}_2\text{O}_4^{2-}$
3	tridentate	dien
4	tetradentate	heme, trien
6	hexadentate	EDTA

Inner and Outer Coordination Sphere and Counter Ions

Example



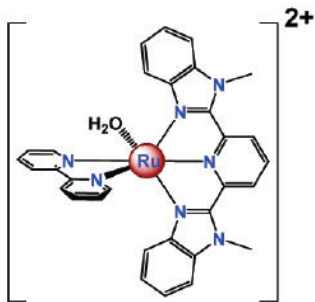
Another example, if needed.



need to change the above structure to have an en ligand instead of two NH_3 's-by

Example Problem

Describe the ligands denticity in this complex ion.

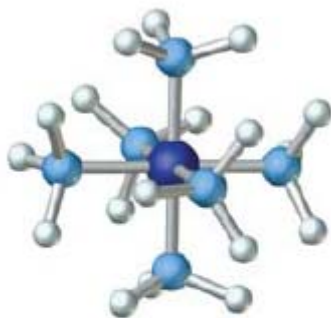


Quick Check Question on Denticity vs. Coordination Number

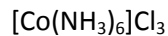
Determining the Central Metal Charge

Determining the charge on the central metal atom is similar to determining oxidation number of an atom in a molecule or ion. The sum of the charges of all parts must add to give the overall charge. In this case, though, ligands are treated as charged units.

Examples: Describe the makeup of these compounds or ions.



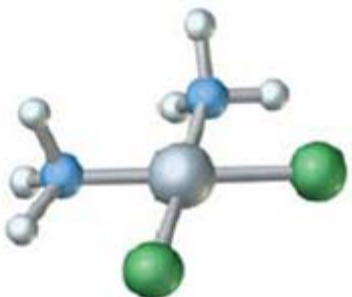
Octahedral
[Co(NH₃)₆]³⁺



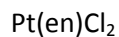
This compound has a Co³⁺ metal center. Each of the NH₃ ligands is neutral. The overall charge is zero. Therefore the Co must match the charge on the three Cl⁻ ions.

$$\begin{array}{r}
 \text{Co} \quad \underline{\quad\quad} \\
 6 \text{ NH}_3 \quad 6 \times 0 \\
 3 \text{ Cl} \quad \underline{3 \times -1} \\
 = 0
 \end{array}$$

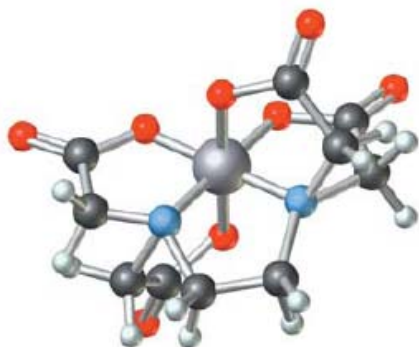
The Co^{3+} metal center is bonded to six monodentate NH_3 ligands. The coordination number is 6. There are three Cl^- counter ions, which are in the outer coordination sphere.



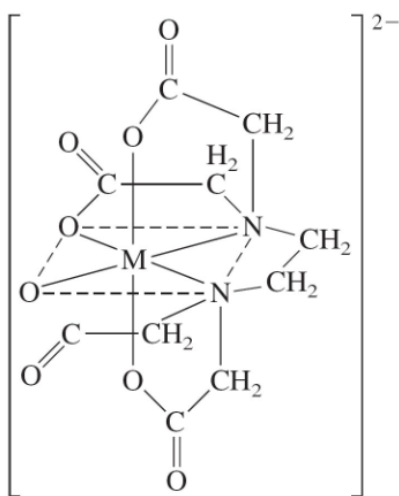
change the two NH_3 into an en ligand



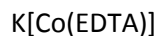
This compound has a Pt^{2+} central metal ion. The en ligand is neutral and the two Cl ligands each possess a -1 charge. The Pt^{2+} metal center is bonded to two monodentate Cl^- ligands and one bidentate en ligand. The coordination number is 4.



moore



zumdahl



This compound has a Co^{3+} metal center. EDTA has a charge of -4. Therefore,

Co _____

EDTA -4

K +1

0

The Co^{3+} metal center is bonded in six positions to the hexadentate EDTA^{4-} ligand. Potassium ion is a counter ion.

22.2b Nomenclature

Susan, I hate this and want you to do it.

aqua

ammine

carbonyl

fluoro, chloro, etc. Hate it.

Example.

22.2c Stability and the Chelate Effect

Chelating ligands make more stable compounds than monodentate ligands that would be expected to form bonds of similar strength to the metal center. Consider the two similar complex ions, $\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}$ and $\text{Cd}(\text{en})_2^{2+}$. Each is 4-coordinate and have very similar metal-ligand bonds, but the former the metal is bonded to four monodentate ligands; in the latter the metal center is bonded to two bidentate ligands. What's the difference? Why should one be more stable than the other?

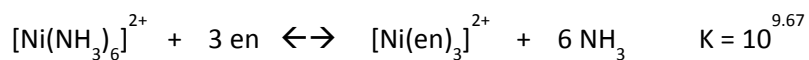
The relative stability of the two compounds can be compared in terms of free energy of formation, ΔG°_f . $\text{Cd}(\text{en})_2^{2+}$ has a free energy of formation that is 23 kJ/mol lower than $\text{Cd}(\text{CH}_3\text{NH}_2)_4^{2+}$, which represents a huge difference in stability. The contributing terms to ΔG°_f , ΔH°_f and $-\text{T}\Delta S^\circ_f$, show a major difference between enthalpy and entropy factors. The table below shows that in terms of enthalpy of formation, the two are indeed nearly identical. Bond strength is not a factor.

Thermodynamics of Formation

Ligands	ΔH° (kJ/mol)	ΔS° (J/K-mol)	$-\text{T}\Delta S^\circ$ (J/mol)	ΔG° (kJ/mol)
4 CH_3NH_2	-57.3	-67.3	20.1	-37.2
2 en	-56.5	+14.1	-4.2	-60.7

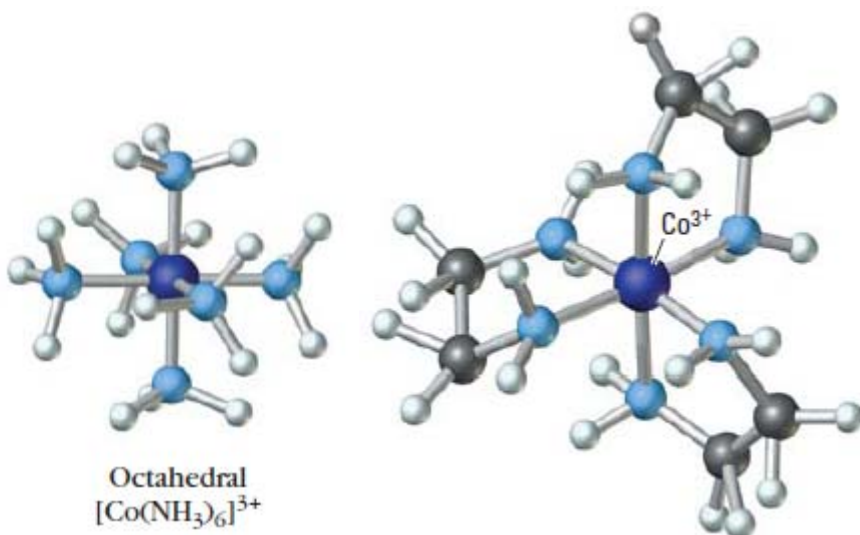
This is called the chelate effect: coordination compounds formed with chelating ligands will be more stable than compounds formed with similar monodentate ligands. The chelate effect is entropy driven.

The chelate effect can also be considered as a competition for of ligands for a metal center. Consider the equilibrium below.

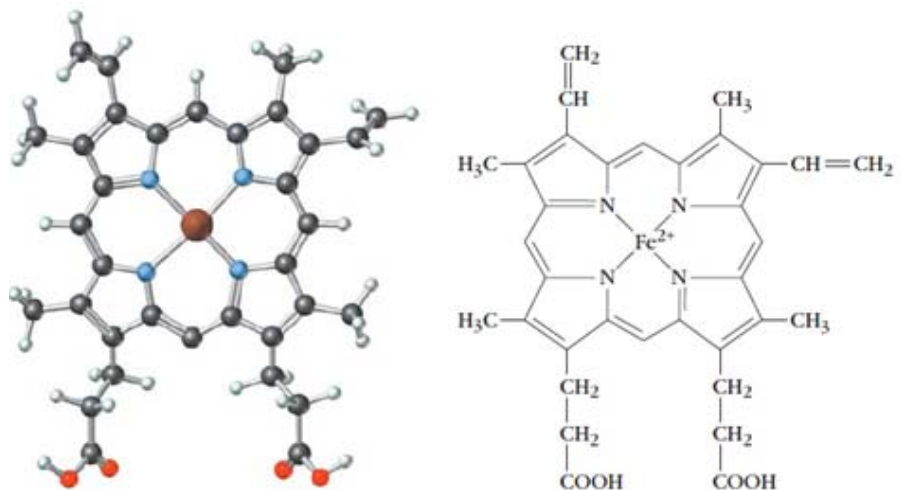


The reactant side has a complex with six monodentate ligands and three unbonded bidentate ligands; four individual particles. The product side has a complex with the metal bonded to three bidentate ligands and six unbonded monodentate ligands; seven individual particles. Because the bond strengths for the different ligands are similar, enthalpy change for the reaction is nearly zero. However, entropy change strongly favors formation of the products due to the greater number of independent species.

Example: Which of the two complex ions below will be more stable in terms of metal-ligand connections?



Macrocyclic ligands provide even more stability. Heme is a good example of this.

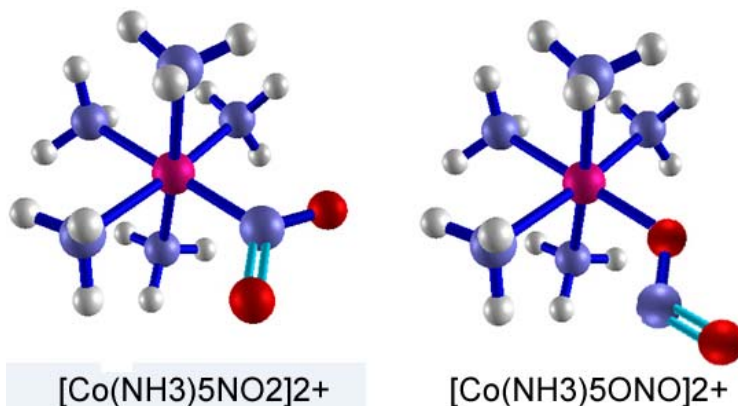


Fe-heme

22.2d Constitutional Isomerism

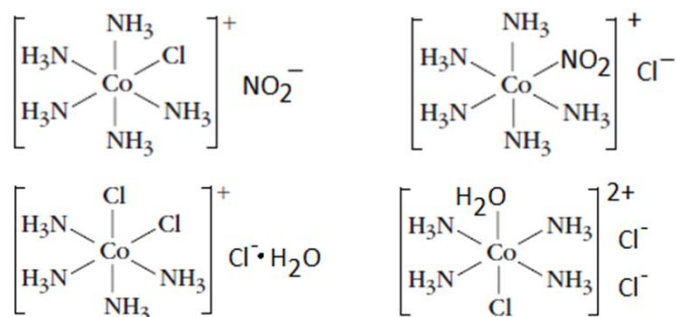
Constitutional isomers are two compounds with the same atoms that differ in their atomic connections. Two of the most important examples constitutional isomerism in coordination compounds are linkage isomerism and hydration isomerism.

Linkage Isomerism



Two coordination compounds that have the same metal center and same ligands, but in which one or more ligands bonds to the metal through different atoms are linkage isomers. In the two compounds shown here, the NO_2 ligand bonds through the N atom in left structure and one of the O atoms in the right structure.

Ionization and Hydration Isomerism



Ionization isomers are two coordination compounds in which two different anions switch positions from the inner sphere and outer sphere. In the example here, the left compound has a Cl^- ligand bonded to the central metal and a NO_2^- counter ion in the outer sphere. In the right structure it is reversed: NO_2^- is a ligand bonded to the metal, and Cl^- is a counter ion in the outer sphere.

CrCl_3 offers a nice colorful example. (VIDEO Module of THIS)

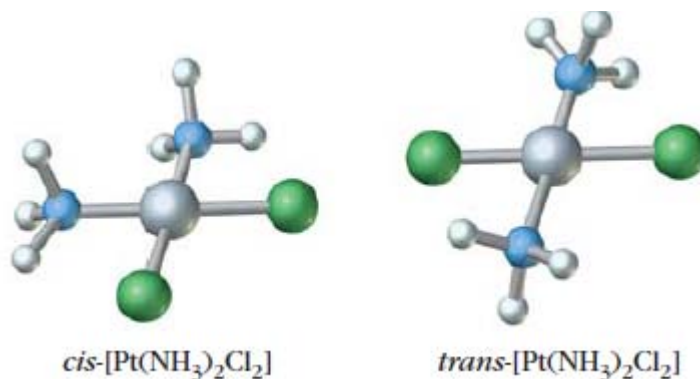
Isomer	Color
$[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$	Violet
$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$	Blue-green
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$	Green

Example: What kind of isomers are these?

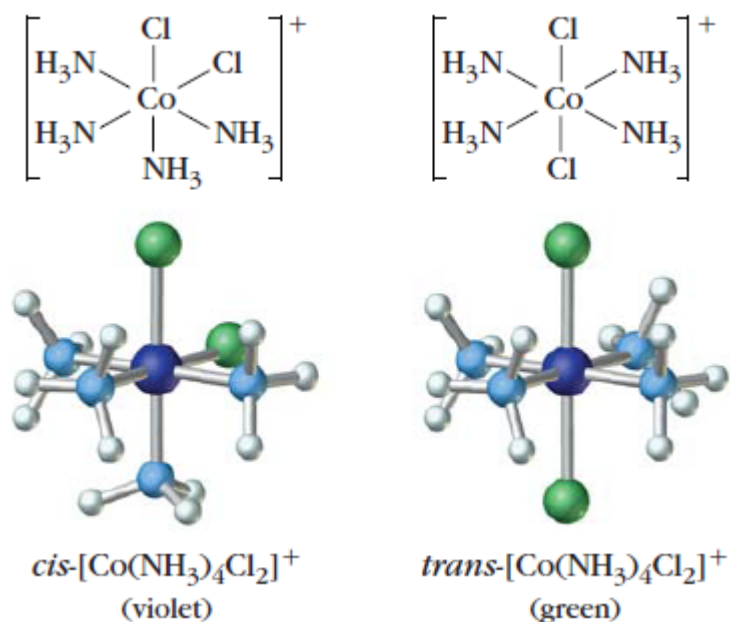
22.2e Stereoisomerism

Stereoisomers are compounds that have the same atoms and the same interatomic connections, but differ the spatial arrangements of the atoms, or in particular here, the ligands. The two most important types of stereoisomers are cis-trans and fac-mer isomerization.

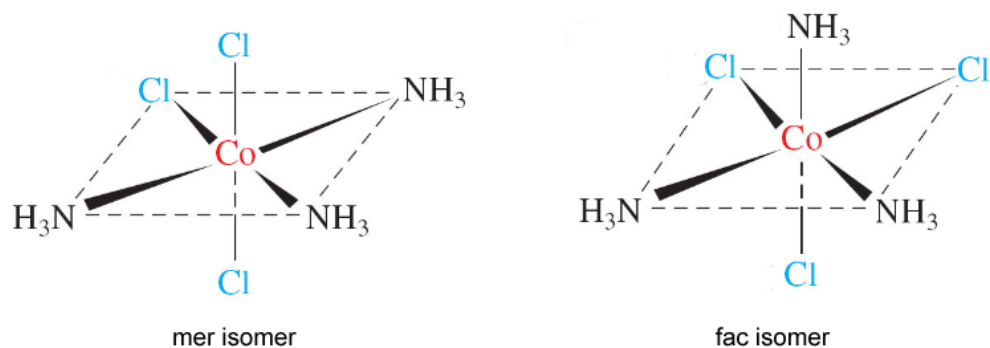
Cis-trans isomers differ in the spatial positions of two ligands. In the cis isomer the ligands are arranged “next to” each other; in the trans case, the two ligands are “across from” each other. A pair of 4-coordinate, square planar cis-trans isomers are shown here. In the cis case the two Cl^- ligands are on the same side of the central Pt atom; in the trans isomer the two Cl^- ligands are directly across from each other.



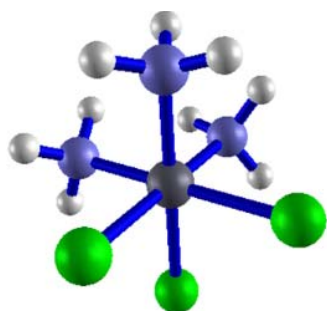
Cis-trans isomerization also occurs in some octahedral compounds. The example below show this.



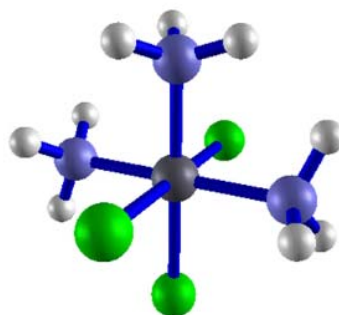
Fac-mer isomerization is similar to cis-trans except it deals with cases where three similar ligands are present. The fac-isomer has three similar ligands on the same face of the octahedron. (****we need an image of this*) The mer-isomer has the three similar ligands in the same plane. The term "mer" comes from meridian, which means ... Fac-mer isomers are mainly observed in 6-coordinate, octahedral compounds.



or use this image:



Fac- isomer



Mer- isomer

optical—skip this, I think.-bv

Example: Are these cis-trans or fac-mer isomers? Is the compound on the left cis, trans, fac, or mer?

22.3 Coordination Compounds: Bonding and Spectroscopy

Section Intro

Among the most impressive aspects of transition metal coordination compounds is the wide range of vibrant colors they exhibit. We have a good understanding of the origin of these colors and what aspects of molecular structure and bonding affect them. In this section we introduce theories of bonding within these compounds, one fairly simple, the other fairly complex. These bonding theories lead us to be able to explain why some compounds are blue, some are red; some are colored brightly, some pale, and others not at all. The technique of measuring the interaction of compounds with visible and ultraviolet light, UV-Vis spectroscopy, is introduced.

Video of different colored solutions being shown or made on the spot.

22.3a d-Electron Configurations

Before considering bonding theories, it is important to remember that bonding interactions between atoms or molecular fragments involve valence orbitals and valence electrons. For our purposes here we will analyze 1st row transition metals, but the concepts translate to the 2nd and 3rd row as well. Transition metals in the 1st row (Sc – Zn, in the 4th period of the periodic table) have electron configuration of the type $4s^23d^x$. When bonded to ligands, the 3d orbitals are at lower energy than 4s orbitals and all the electrons can be considered occupy 3d orbitals. The d electron configuration is determined by counting the total number of 4s and 3d electrons based on periodic position, and adjusting for charge.

Examples:



Fe is $4s^23d^6$, which is 8 electrons. Subtract 2 for the 2+ charge, and get d^6 .

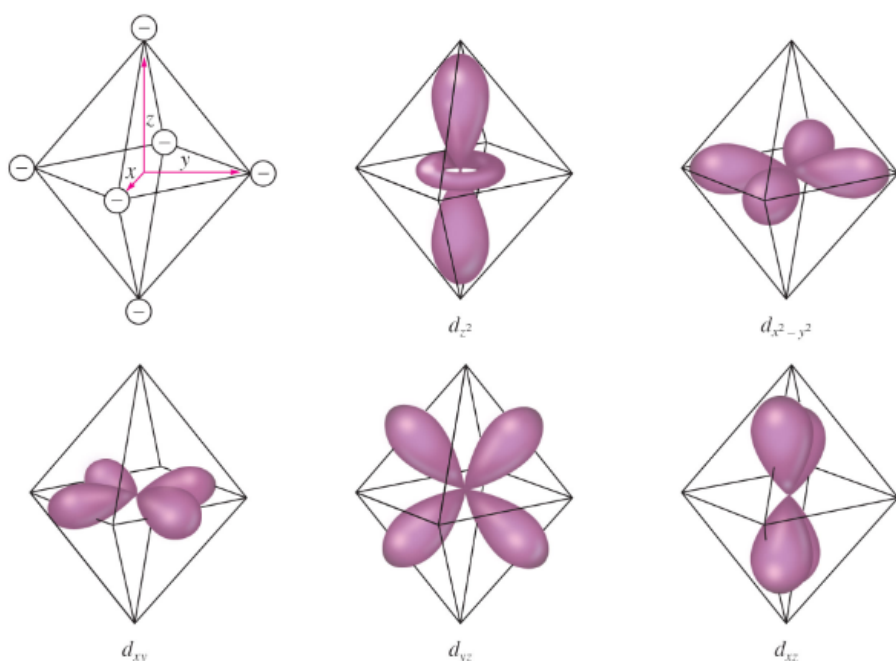
Co^{2+}

Co is $4s^23d^7$, which is 9 electrons. Subtract 2 for the 2+ charge and get d^7 .

22.3b Crystal Field Theory

To be added by Susan. I have placed the hs/l's stuff here, but you might move it. I've added a useful CFT figure below.

I assume the following are introduced: eg/t2g names for the octahedral orbital sets (just as names) and Δ_o .



zumdahl

Quick Check Questions For This

High and Low Spin Electron Configurations

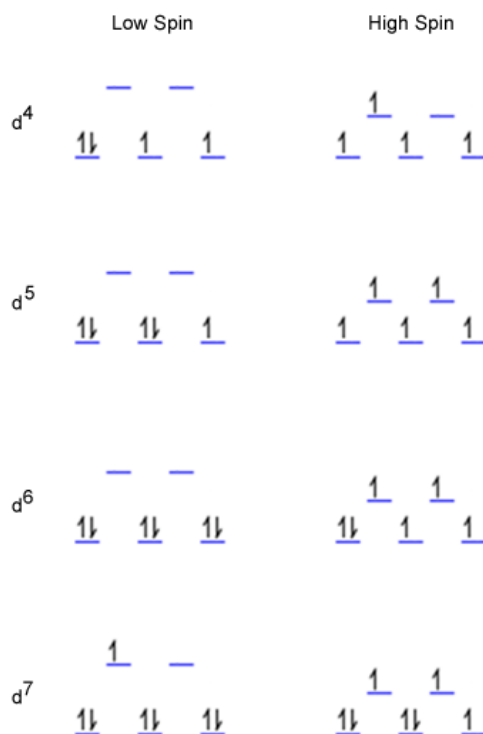
When electrons fill d orbitals that exist at two (or more) different energies, two energetic factors come into play: the native energy of the orbital and the degree to which electron-electron repulsions destabilize an electron when added to a particular orbital. This latter factor is mainly important when filling a second electron into an orbital already occupied by one electron. In cases where the energy gap between the two sets of orbitals is small, the electron is more stable filling a vacant orbital at higher energy than it is filling a partially occupied orbital at lower energy.

Consider the addition of the last electron in a d^4 complex. The first three electrons clearly will fill the lower t_{2g} set of d orbitals with a single electron in each, so as to keep electrons as far from one another as possible to minimize electron-electron repulsions. When the fourth electron is added to a compound with a large d-d energy gap, it fills into the lower energy t_{2g} orbitals. Even though the pairing up of electrons in a single orbital leads to greater repulsions, this is a smaller price to pay than filling the much higher energy e_g orbitals. This configuration has a total of two unpaired electrons and is called the low spin configuration.



Now consider the case where the d-d energy gap is small. In this case the energy disadvantage of filling the e_g orbitals is smaller than that of pairing with another electron in a t_{2g} orbital. This configuration has four unpaired electrons and is called the high spin configuration.

Figure 22.XXX shows the distinct high and low spin states are possible for d^4 , d^5 , d^6 , and d^7 electron configurations of octahedral compounds. All other d-electron configurations do not have distinct high spin/low spin states.

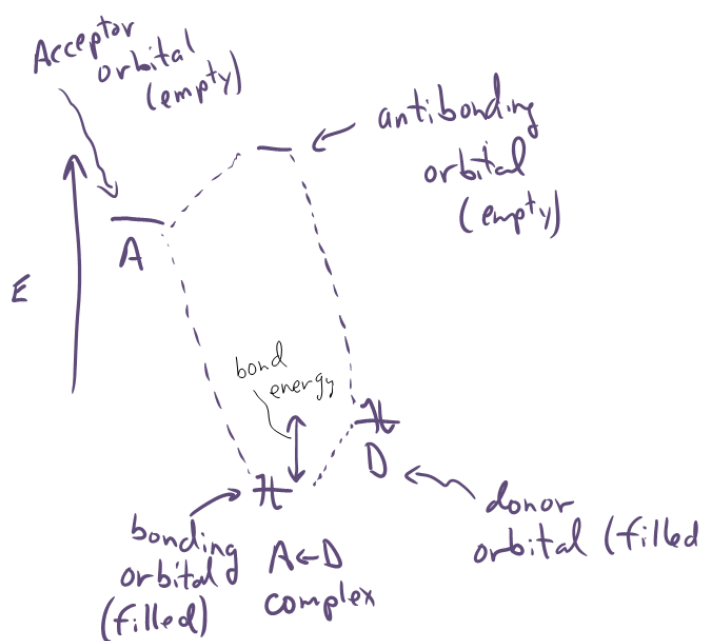


Example

22.3c Molecular Orbital Theory

The crystal field theory is useful for explaining the occurrence of splitting between sets of metal d orbitals in a coordination complex. It pretty much end there, though. The idea of purely electrostatic interactions provides predictions of relative interaction strength that are often exactly opposite of what occurs. For example, when comparing the d-orbital splitting caused by NH_3 , H_2O , and OH^- ligands, crystal field theory would predict OH^- (with a full negative charge) to lead to the largest effect, and NH_3 (with a smaller partial negative charge than on the O atom of H_2O) to have the smallest. Instead, the order of d-orbital splitting is $\text{NH}_3 > \text{H}_2\text{O} > \text{OH}^-$. In fact, among the strongest ligands is carbon monoxide, CO , which bonds through its C atom, which has little or no negative charge. It would be expected to lead to no splitting at all.

A more useful and accurate model is based on molecular theory. In this case, bonding atoms are treated as Lewis acids (electron acceptors) or Lewis bases (electron donors). The general MO diagram for a donor-acceptor interaction is shown in Figure 22.XXX.



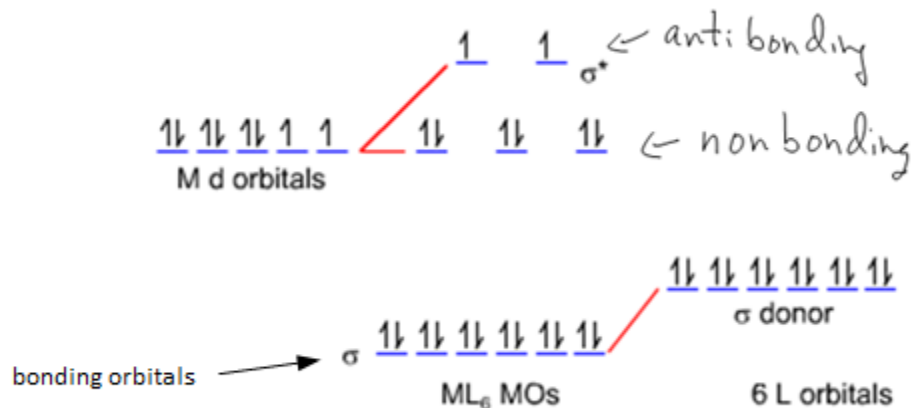
Donor \rightarrow Acceptor MO Diagram

When the donor lone pair orbital overlaps the vacant acceptor orbital, two new orbitals are formed: a bonding orbital at lower energy and an antibonding orbital at higher energy. Although not strictly accurate, it is convenient to think that when a donor-acceptor interaction occurs, the donor orbital moves lower in energy and becomes a bonding orbital and the acceptor orbital moves higher in energy and becomes an antibonding orbital.

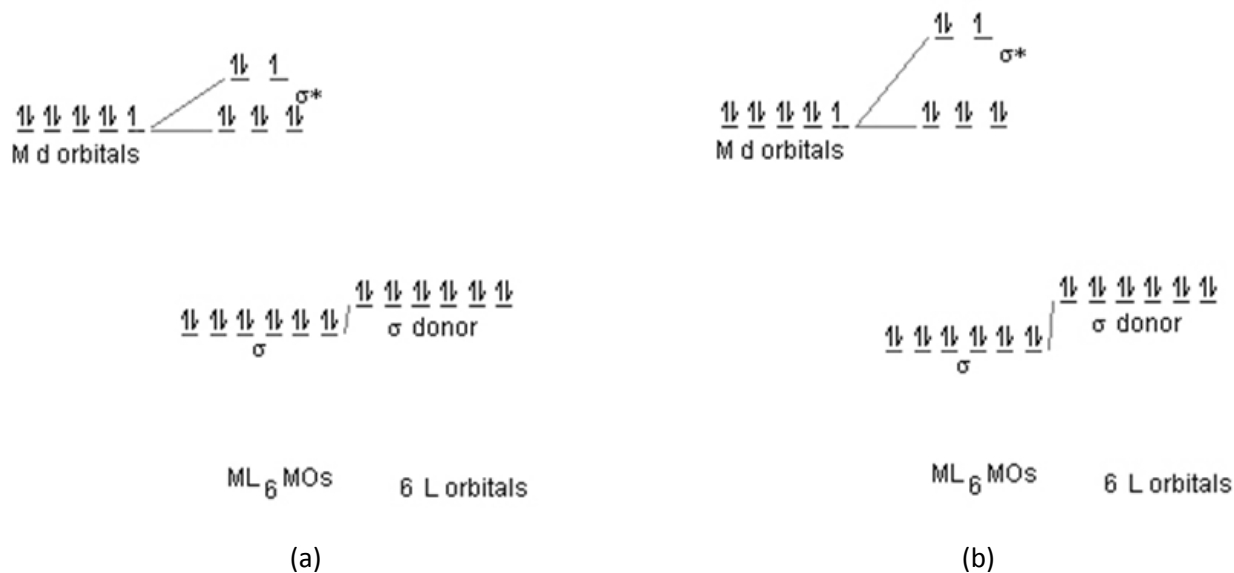
QuickCheck Question

Octahedral Complexes with Ligands that form only Sigma Bonds

All ligands act as sigma electron-pair donors, and each ligand donor orbital in a complex decreases in energy. These are the basis of the bonding of the ligands to the metal. However, not all of the metal orbitals act the same way. When a set of six ligands surround a metal, sigma interactions occur between the metal's d_{z^2} and $d_{x^2-y^2}$ orbitals, but not the other three d orbitals (d_{xy} , d_{xz} , and d_{yx}). Because of this, two d orbitals move up in energy and three remain at the same energy (and are called nonbonding orbitals). Figure 22.XXX shows an MO diagram for a typical ML_6 octahedral complex.



What about two ligands where one has a stronger interaction with the metal d orbitals? Figure 22. XXX shows a weak interaction case (a) and a strong interaction case (b).



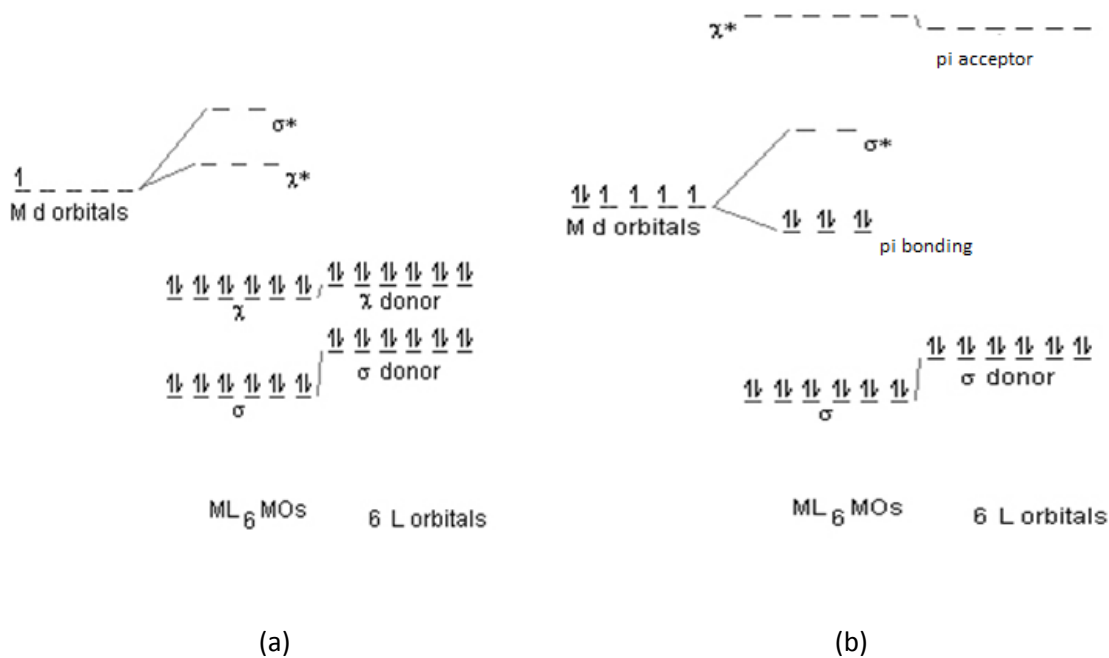
The donor orbitals of the more strongly interacting ligand will decrease in energy and be more strongly bonding than those of the weakly interacting ligand. At the same time, the metal d orbitals in the strongly interacting case will increase in energy more, and become more strongly antibonding. The overall strength of the metal ligand interaction depends on the degree to which the donor orbitals

decrease in energy, the degree to which the metal sigma orbitals increase in energy, and the number of electrons occupying the metal antibonding orbitals.

Octahedral Complexes with Ligands that form Sigma and Pi Interactions

Many ligands act as sigma electron-pair donors but also have pi interactions with the metal. Some ligands act as pi electron donors. The most important of these are OH^- , $\text{C}_2\text{O}_4^{2-}$, and O^{2-} . In an octahedral complex, pi interactions occur with the metal d orbitals that did not show sigma interactions: d_{xy} , d_{xz} , d_{yz} . Figure 22.XXXa shows an MO diagram for an octahedral complex containing ligands that are both sigma and pi donors. Both ligand sigma and pi donor orbitals decrease in energy to form bonding orbitals. Both sets of metal d orbitals are acceptors, and as such, increase in energy to become antibonding. Sigma interactions are generally stronger than pi interactions, and so the sigma d orbitals (d_{z^2} and $d_{x^2-y^2}$) move higher in energy than do the pi d orbitals (d_{xy} , d_{xz} , d_{yz}).

Figure 22.XXXb shows an MO diagram for an octahedral complex that has ligands that are sigma donors (as are all ligands) and pi acceptors. The most important pi acceptor ligands are CO, CN^- , and triphenylphosphine, PPh_3 . Each of these ligands contains an empty, high energy orbital that can accept electron density from a metal d orbital in a pi interaction. Notice that in this case the metal pi d orbitals (d_{xy} , d_{xz} , d_{yz}) are now the donor orbitals. They, like all donor orbitals, move lower in energy while the metal sigma d orbitals (d_{z^2} and $d_{x^2-y^2}$) are acceptors and move higher in energy. The vacant ligand pi orbitals move higher in energy.

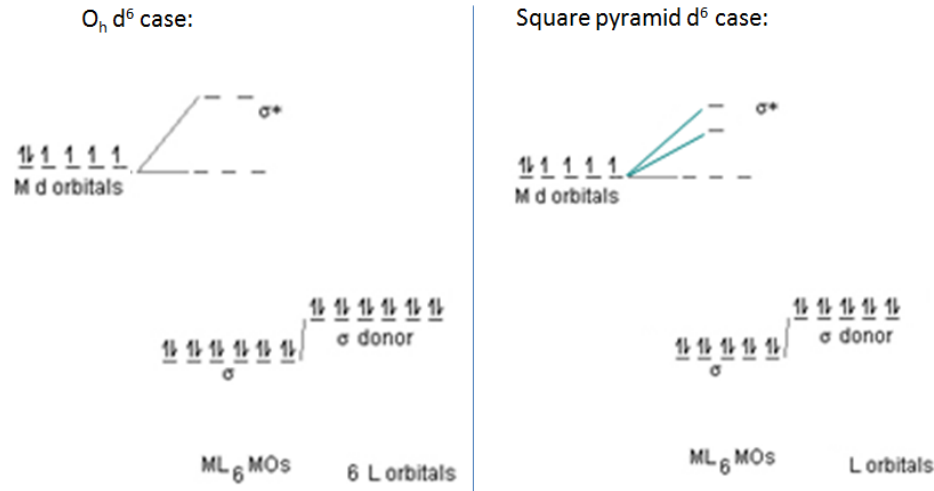


NOTE: The pi symbols in these look like "x" and need to be pi symbols.

Exercise analyzing the MO diagrams.

Other Geometries

MO diagrams can be generated for many different metal-ligand geometries. Four are shown here, each assuming the same strength of metal-ligand interaction.



22.3d Spectroscopy

do we want the color wheel?? I really don't like the color wheel thing. I'd rather show spectra and photos of the solutions so you can see how they relate.-bv

UV-Vis Spectroscopy is a technique that analyzes how much light a solution absorbs as a function of wavelength. The plot of absorbance vs. wavelength is called a spectrum (the plural of which is "spectra.") Most chemical compounds absorb light in the visible and/or ultraviolet region by promoting an electron from a lower energy orbital to one of higher energy. As such, measurements of the energy of light absorbed tells us about the spacing between different orbitals in a compound.

The wavelengths absorbed also relate to the colors we observe by eye. When red light is absorbed, the solution appears blue. When blue light is absorbed, the solution appears red.

Figure 22.XXX shows a diagram of a diode-array UV-Vis spectrometer.

spectrometer

White light of all wavelengths passes through a sample, and then encounters a diffraction grating. The diffraction grating acts like prism, separating the light into its constituent wavelengths. The spread out rainbow of light then falls upon a series of photodiodes (one might say an array of diodes). The position of each diode determines what wavelength it is measuring. The amount of current it produces indicates

how much light of that wavelength is striking the diode. The more light striking the diode, the less that was absorbed by the sample. The amount of light hitting the diode with the sample in place (I) is compared with that in the absence of the sample (I_0). The sample's absorbance at that wavelength is given by,

$$\text{Absorbance} = -\log \frac{I}{I_0}$$

If the sample absorbs 90% of the light, Abs = 1.0; if it absorbs 99% of the light, Abs = 2.0.

Example of this? Or QuickCheck

Figure 22.XXX shows the spectrum of ????.

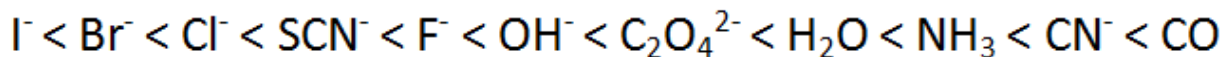
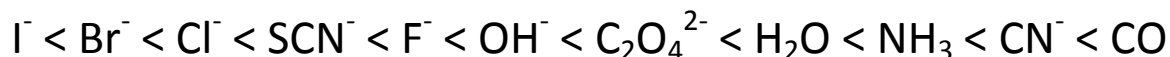
d-d Transitions

Many transition metal compounds absorb visible light in a process that promotes a d electron from the low energy t_{2g} orbitals to the higher energy e_g d orbitals. These electronic transitions are called d-d transitions, and the colors of many complexes can be explained by this transition, their electron configurations, and their relative Δ_o energy gaps. The relative size of Δ_o is a direct result of the degree of metal ligand sigma interaction and whether any pi interactions occur. The following general trends occur:

Strong sigma interaction	Weak sigma interaction	Pi donor ligands	Pi acceptor ligands
Lead to larger Δ_o	Lead to smaller Δ_o	Lead to smaller Δ_o	Lead to larger Δ_o
Absorb shorter wavelengths	Absorb longer wavelengths	Absorb longer wavelengths	Absorb shorter wavelengths
Favor low spin states	Favor high spin states	Favor high spin states	Favor low spin states

These trends are collected in a ranking of the tendency of particular ligands to lead to large or small values of Δ_o , called the spectrochemical series. The further right on the series, the larger Δ_o gap a ligand will lead to.

Spectrochemical Series



pi donor ligands

sigma only
ligands

pi acceptor
ligands

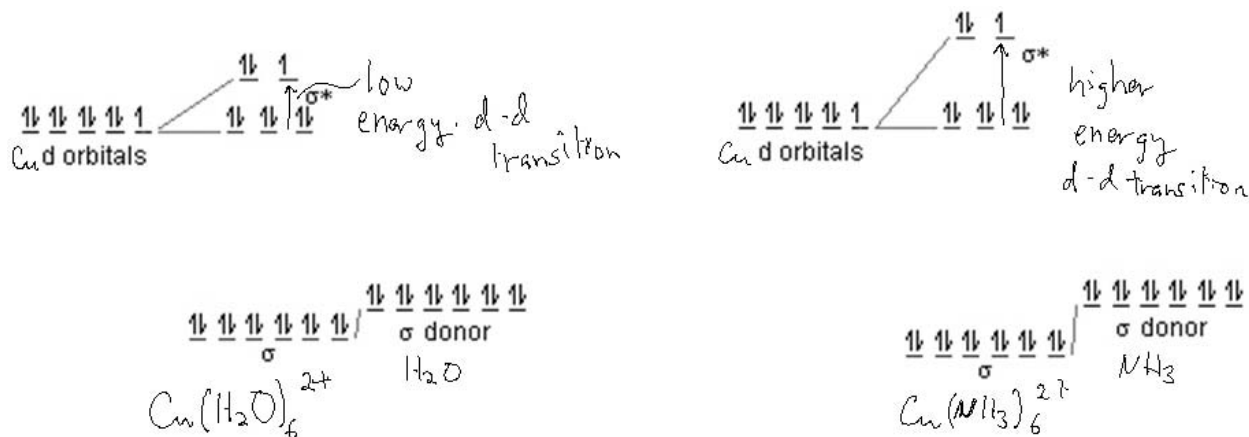
---The above needs a bit more work- OH- vs. H₂O is due to pi donation, but are the halides low because of weak sigma interaction or because of pi donation? Both fit and I don't know which is true.-bv

----Add something about the effect of metal charge??? Co³⁺ absorbs at higher E than Co²⁺, etc.???

We consider four cases of transition metal complex colors that depend on d-d transitions.

Why is Cu(NH₃)²⁺ dark blue but Cu(H₂O)²⁺ is pale blue?

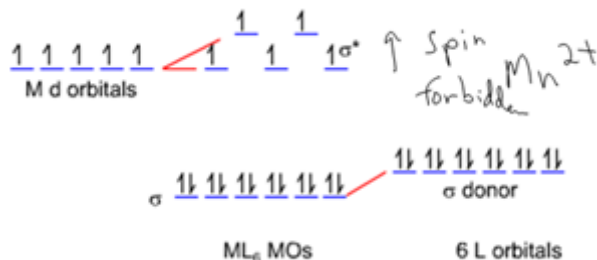
Because NH₃ is a stronger sigma-donor ligand. This leads to a larger Δ_o energy gap, and absorption of mostly red light (causing the compound to look blue). H₂O is a weaker ligand, leads to a small Δ_o energy gap, and absorption of mostly infrared light at wavelengths beyond 700 nm.



Need to add spectra.

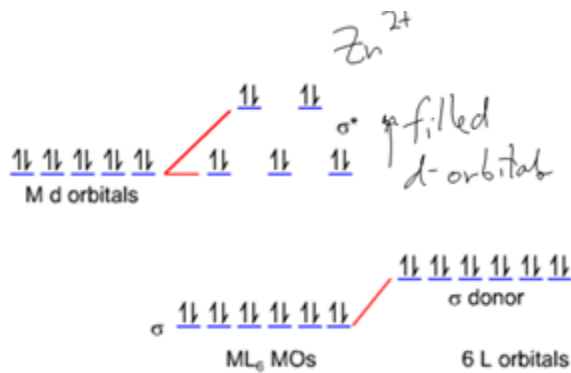
Why is Mn²⁺(aq) colorless?

Because it is d⁵ high spin and the d-d transition is spin forbidden.



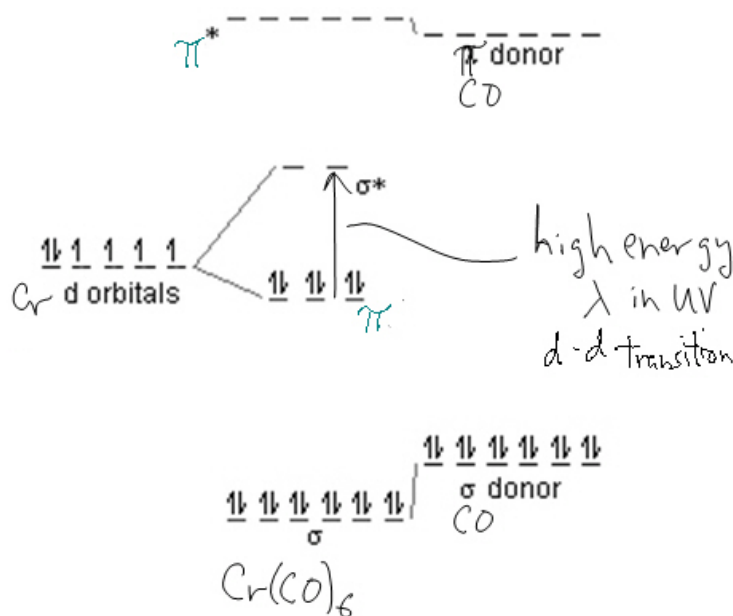
Why is Zn²⁺(aq) colorless?

Because it has a d¹⁰ configuration, all the d orbitals are filled, and no d-d transition can take place.



Why is $Co(CO)_6$ colorless?

Because CO is such a strong pi acceptor ligand it leads to a Δ_o energy gap so large that the light absorbed is shorter than 400 nm and is in the UV.



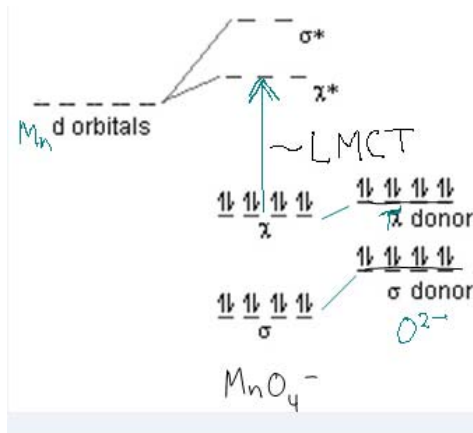
Need to add spectrum showing abs. in the UV.

Other Transitions

Some compounds make no sense in terms of d-d transitions. For example, permanganate ion, MnO_4^- , is formally a d^0 ion. If no d orbitals are occupied, no d-d transitions can take place. Yet MnO_4^- is deeply purple in color. The absorption that leads to this color arises from a transition from an oxygen-based orbital up to a vacant Mn d orbital. This transition is called a ligand-to-metal transition, or LMCT.

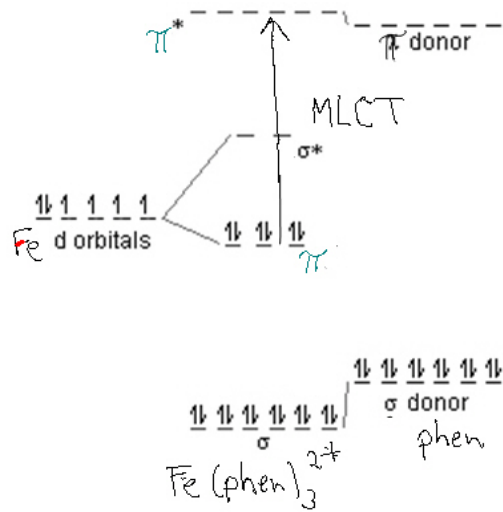
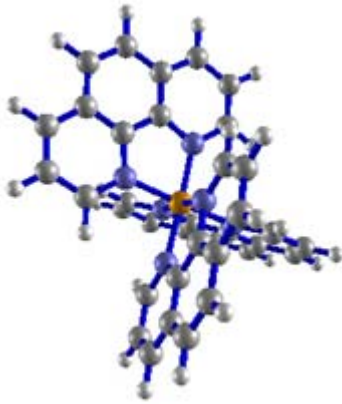
LMCT

MnO₄⁻



MLCT

Fe(phen)₃²⁺



$\text{Fe}(\text{phen})_3^{2+}$ MLCT. *make video of adding phen to Fe^{2+} solution.*

22.4 Reactivity

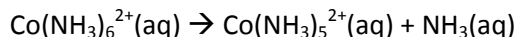
Section Intro

The most important commercial reactions of transition metal compounds are oxidation-reduction reactions, most important of all being the reduction of metal ores to form neutral metals explored in Section 22.1. However, the most interesting and studied aspects of transition metal chemistry involve gain, loss, and replacement of ligands. These reactions are the core basis for synthesizing the wide range of compounds known and the pathway to creating compounds with specific, desired properties. Many of these reactions happen in biological systems as well as in the laboratory.

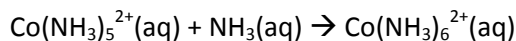
Module: *animations of different reaction mechanisms*

22.4a Ligand Dissociation, Addition, and Substitution

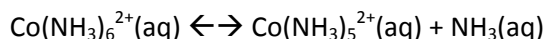
The simplest of reactions a transition metal complex can undergo is ligand dissociation. This reaction involves the simple breaking of one of the metal–ligand bonds.



Ligand addition is the opposite reaction, where a new metal-ligand bond is formed.



As implied in these two examples, ligand loss and gain reactions are often part of reversible equilibria.

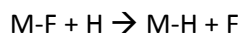


Of greater interest is the loss of one ligand followed by the addition of a different ligand. This pair of events result in a ligand substitution reaction.



Mechanisms of Ligand Substitution: Mechanisms are a lot like love.

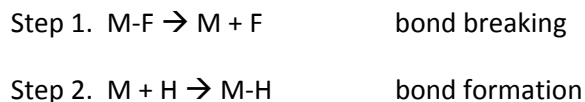
Mechanisms are a lot like love, and the ruination and rebirth thereof. Consider the reaction of a male-female couple (M-F) with an unbonded woman (we'll call her H, for harlot). The products of this reaction are a new couple, M-H, and a newly unbonded woman, F.



This reaction can take place via two different mechanisms.

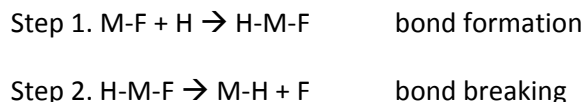
Dissociative Mechanism

In a dissociative mechanism, the relatively unstable couple, M-F, undergoes a dissociative mechanistic step. After this step, M is free to bond with a different mate, and so he does in step 2.



Associative Mechanism

In an associative mechanism, the first step is the formation of an unstable 3-body transition state where M is associated with both F and H. This unstable transition state decomposes to form the products.



Interestingly, the rate of the dissociative mechanism is independent of the concentration of available harlots, [H], but is directly proportional to the concentration of couples. This gives a first order rate law:

$$\text{Rate} = k[M-F]$$

The rate of the associate mechanism is a second order process, depending on the concentration of couples as well as available harlots. This gives a second order rate law:

$$\text{Rate} = k[M-F][H]$$

Which mechanism generally prevails depends on which planet one lives on, and we all know which one we do.

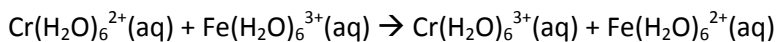
It's the same way for coordination compound substitution reactions.

22.4b Oxidation-Reduction Reactions

Transition metals are interesting in that they often display multiple stable oxidation states. For example, iron has many Fe^{2+} compounds and many Fe^{3+} compounds. The same is true for many of the transition metals. We consider two examples of oxidation-reduction reactions in coordination compounds, one of chemical interest, the other of commercial interest.

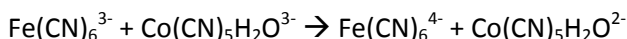
Mechanisms of Simple Electron Transfer Reactions

The simplest oxidation-reduction reactions are those that involve the transfer of a single electron from one reactant to another. The compound losing an electron is oxidized; the compound gaining an electron is reduced. An example is the reaction of $\text{Cr}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$.

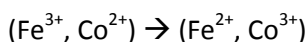


Electron transfer reactions occur by one of two mechanisms, inner sphere or outer sphere. In an outer sphere mechanism, the two reactants approach each other, the electron jumps from one to the other, and they float apart. The reaction above happens that way. Just that simple.

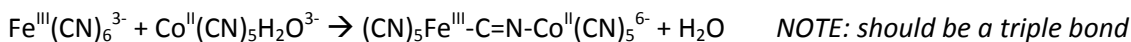
In an inner sphere reaction, before the electron transfer can take place a ligand bridge is formed between the two reacting metal centers. Consider,



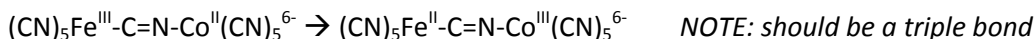
Recalling that the cyanide ligand has a 1- charge, the reaction involves changes in oxidation states from



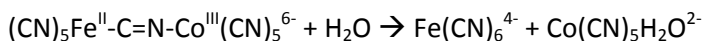
The first step of the reaction involves loss of the weakly bonded H_2O ligand and formation of a CN bridge. This creates a relatively long-lived intermediate,



The second step is the electron transfer step,



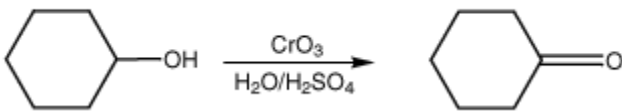
Finally, the bridged intermediate dissociates and a H_2O ligand fills the vacant coordination slot on the Co atom,



Metal oxide oxidizing agents.

The most important aspect of coordination compound oxidation-reduction reactivity involve the use of metal oxides and oxoanions as oxidizing agents. These compounds contain metals in very high oxidation states and they are good electron acceptors as well as good oxygen atom transfer agents. Some of the more important uses are given in the following table:

Reagent	Metal Product	Transformation
CrO_4^{2-}		Oxidation of aldehydes to carboxylic acids.

		<p>ethanal (acetaldehyde)</p> $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \xrightarrow{\text{H}_2\text{CrO}_4} \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ <p>acetic acid</p>
CrO ₃		<p>Oxidation of a secondary alcohol to a ketone.</p> <p>cyclohexanol</p>  <p>cyclohexanone</p>
MnO ₄ ⁻		<p>Oxidation of alkenes to ketones or carboxylic acids.</p> <p>2-methyl-2-butene</p> $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{H} \end{array} \xrightarrow[\text{H}_3\text{O}^+]{\text{KMnO}_4} \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{CH}_3 \\ \text{acetic acid} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{OH} \\ \text{carbon dioxide} \end{array}$ <p>propene</p> $\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \xrightarrow[\text{H}_3\text{O}^+]{\text{KMnO}_4} \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{OH} \\ \text{acetic acid} \end{array} + \text{CO}_2$
OsO ₄		<p>Addition of two oxygen atoms across a C=C double bond.</p> <p>propene</p> $\begin{array}{c} \text{CH}_3 \quad \text{H} \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \xrightarrow[\text{H}_2\text{O}_2]{\text{OsO}_4} \begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{CH}_3-\text{C}-\text{C}-\text{H} \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$ <p>1,2-propanediol</p>

does anyone even know what the metal products are of these reactions?

4.3c Reaction of a Bonded Ligand

I can't think of an example, so feel free to add one or delete this section.

=====

Common Oxidation States of Transition Metals

■ **Table 25-1** Common Oxidation States and *d*-Electron Counts for the Transition Metals

Sc +3 <i>d</i> ⁰	Ti +3 <i>d</i> ¹ +4 <i>d</i> ⁰	V +3 <i>d</i> ² +5 <i>d</i> ⁰	Cr 0 <i>d</i> ⁶ +2 <i>d</i> ⁴ +3 <i>d</i> ³ +4 <i>d</i> ² +6 <i>d</i> ⁰	Mn +1 <i>d</i> ⁶ +2 <i>d</i> ⁵ +3 <i>d</i> ⁴ +5 <i>d</i> ² +7 <i>d</i> ⁰	Fe 0 <i>d</i> ⁸ +2 <i>d</i> ⁶ +3 <i>d</i> ⁵	Co 0 <i>d</i> ⁹ +1 <i>d</i> ⁸ +2 <i>d</i> ⁷ +3 <i>d</i> ⁶	Ni 0 <i>d</i> ¹⁰ +2 <i>d</i> ⁸	Cu +1 <i>d</i> ¹⁰ +2 <i>d</i> ⁹	Zn +2 <i>d</i> ¹⁰
Y +3 <i>d</i> ⁰	Zr +4 <i>d</i> ⁰	Nb +3 <i>d</i> ² +5 <i>d</i> ⁰	Mo 0 <i>d</i> ⁶ +2 <i>d</i> ⁴ +4 <i>d</i> ² +6 <i>d</i> ⁰	Tc +1 <i>d</i> ⁶ +3 <i>d</i> ⁴ +5 <i>d</i> ² +7 <i>d</i> ⁰	Ru 0 <i>d</i> ⁸ +2 <i>d</i> ⁶ +3 <i>d</i> ⁵	Rh 0 <i>d</i> ⁹ +1 <i>d</i> ⁸ +2 <i>d</i> ⁷ +3 <i>d</i> ⁶	Pd 0 <i>d</i> ¹⁰ +2 <i>d</i> ⁸ +4 <i>d</i> ⁶	Ag +1 <i>d</i> ¹⁰	Cd +2 <i>d</i> ¹⁰
La +3 <i>d</i> ⁰	Hf +4 <i>d</i> ⁰	Ta +3 <i>d</i> ² +5 <i>d</i> ⁰	W 0 <i>d</i> ⁶ +2 <i>d</i> ⁴ +4 <i>d</i> ² +6 <i>d</i> ⁰	Re +1 <i>d</i> ⁶ +2 <i>d</i> ⁵ +3 <i>d</i> ⁴ +5 <i>d</i> ² +7 <i>d</i> ⁰	Os 0 <i>d</i> ⁸ +2 <i>d</i> ⁶ +3 <i>d</i> ⁵	Ir 0 <i>d</i> ⁹ +1 <i>d</i> ⁸ +2 <i>d</i> ⁷ +3 <i>d</i> ⁶	Pt 0 <i>d</i> ¹⁰ +2 <i>d</i> ⁸ +4 <i>d</i> ⁶	Au +1 <i>d</i> ¹⁰ +2 <i>d</i> ⁹ +3 <i>d</i> ⁸	Hg +2 <i>d</i> ¹⁰

When Lewis bases bond to a transition metal, the *d* orbitals always fill before the next higher *s* orbital. The filled noble gas electron configuration associated with each transition metal is usually omitted and just the valence *d*-electron count is shown.

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■ **Table 23-7** Nonzero Oxidation States of the 3*d*-Transition Metals*

3B	4B	5B	6B	7B	8B			1B	2B
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1 r	
				+2	+2 r	+2	+2	+2	+2
+3		+3 r	+3		+3	+3 o			
	+4	+4		+4 o					
		+5 o							
			+6 o						
				+7 o					

*Abbreviations: o = oxidizing agent; r = reducing agent.

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