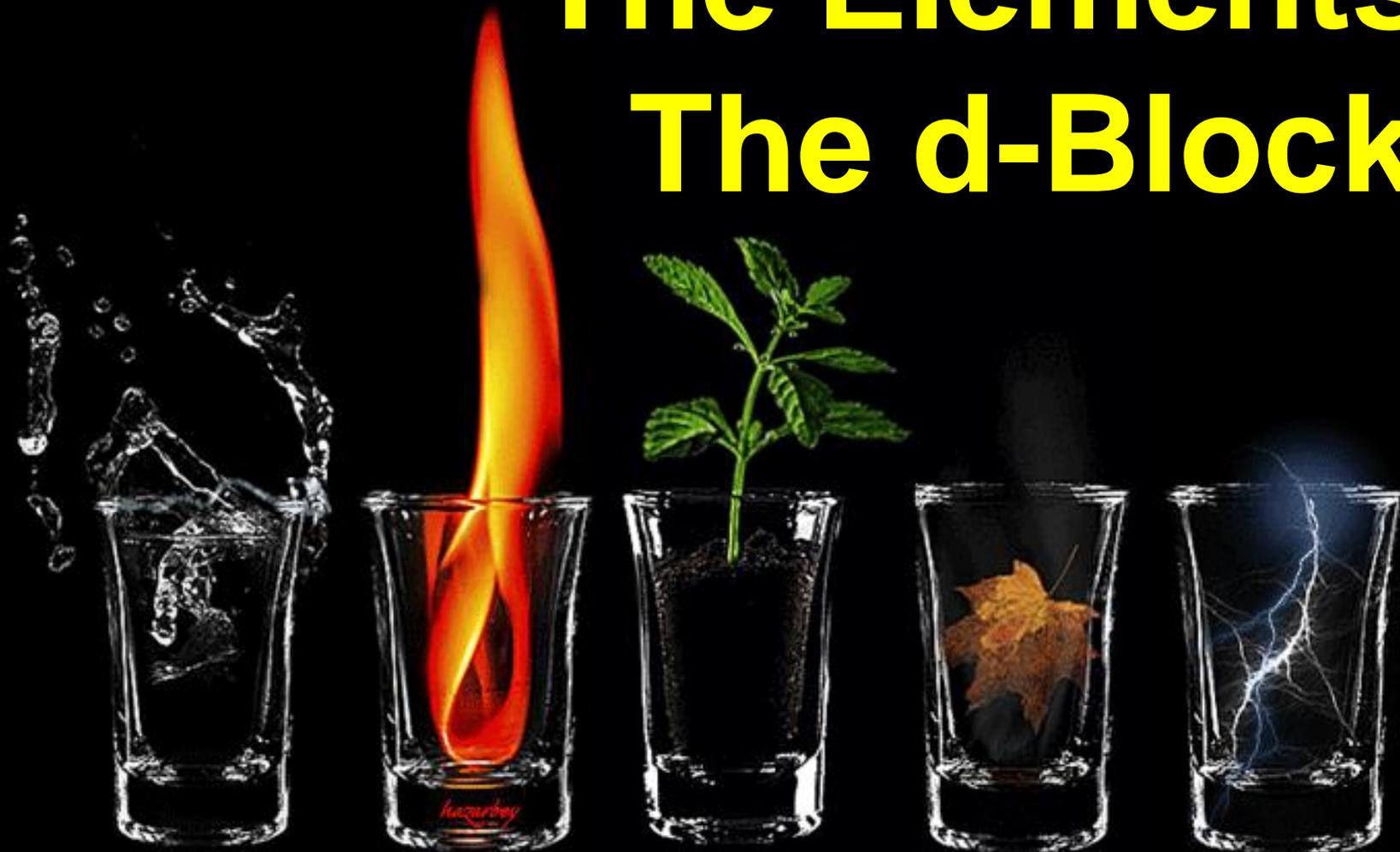
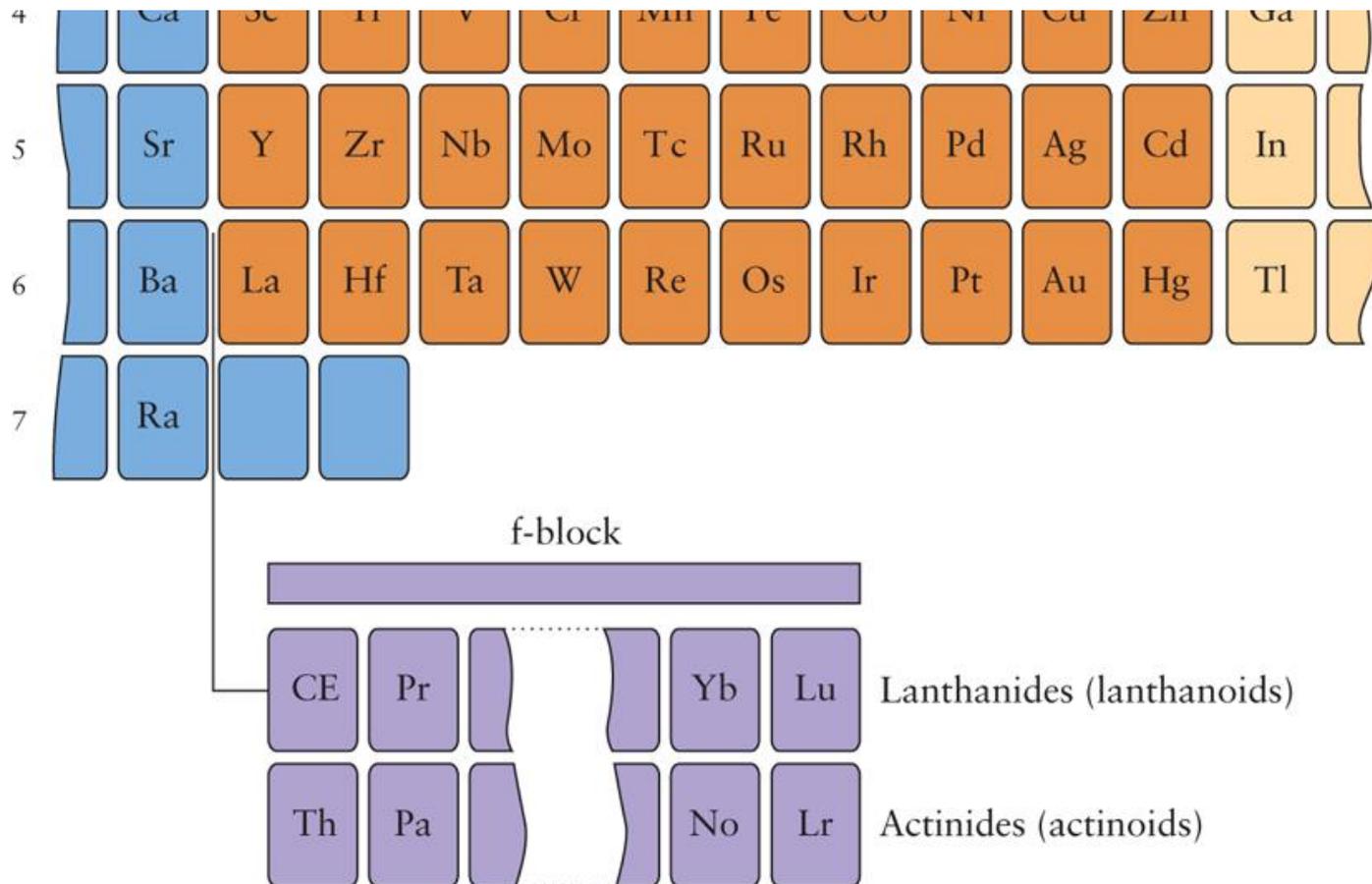


The Elements: The d-Block



The f-Block Elements

Inner transition metals, lanthanoids and actinoids, fill after the 6 and 7 s respectively.



Physical Properties

Notice the similarities in their physical properties like:

- melting points;
- boiling points;
- changes to density; and
- resistance to corrosion.

Z	Name	Symbol	Valence electron configuration	Melting point (°C)	Boiling point (°C)	Density, (g·cm ⁻³)
21	scandium	Sc	3d ¹ 4s ²	1540	2800	2.99
22	titanium	Ti	3d ² 4s ²	1660	3300	4.55
23	vanadium	V	3d ³ 4s ²	1920	3400	6.11
24	chromium	Cr	3d ⁵ 4s ¹	1860	2600	7.19
25	manganese	Mn	3d ⁵ 4s ²	1250	2120	7.47
26	iron	Fe	3d ⁶ 4s ²	1540	2760	7.87
27	cobalt	Co	3d ⁷ 4s ²	1494	2900	8.80
28	nickel	Ni	3d ⁸ 4s ²	1455	2150	8.91

Physical Properties

All the d-block elements are **metals**.

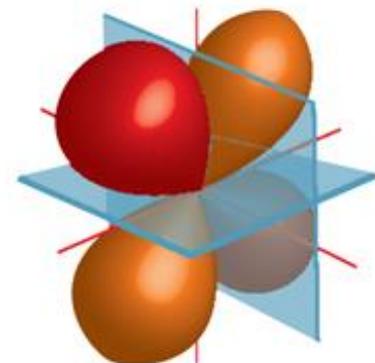
Most are good electrical conductors-**silver** is the best *electrical conductor* of all elements.

Most are *malleable, ductile, lustrous, and silver white in color*, the **exceptions**: **copper** is red-brown, **gold** is yellow, and **mercury** is a liquid at room temperature.

Their *melting and boiling points are higher*,

d-orbitals lobes effect the properties in two ways:

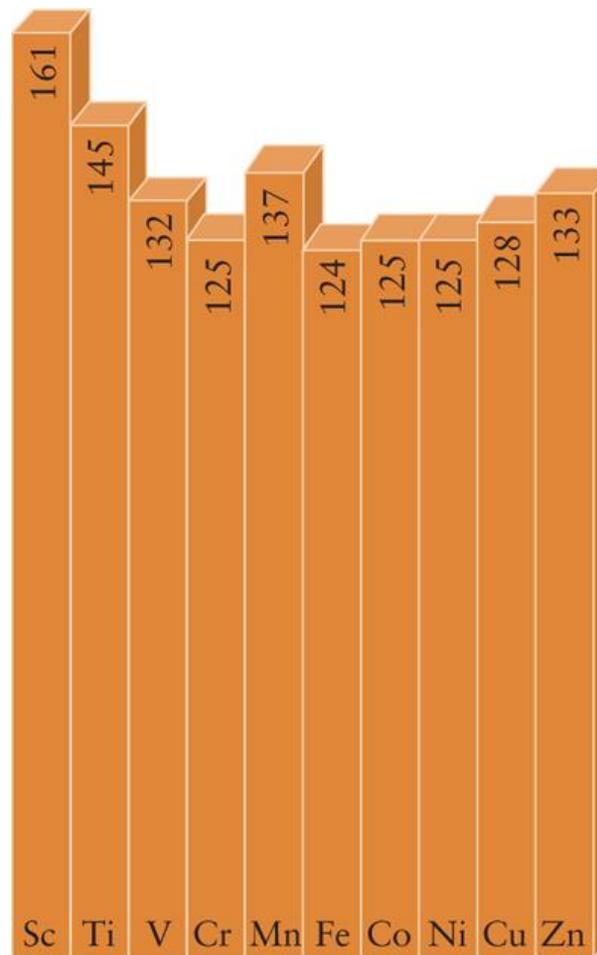
- 1.) electrons in the lobes are far apart and weakly repelling each other.
- 2.) d-orbitals are poor at shielding because their electron density is low near the nucleus.



Physical Properties

Atomic radii **decrease** then increase due to lack of shielding from d-orbitals.

Additional d-electrons **increase electron-electron repulsions** more rapidly, than nuclear charge increases, so the radii increase.



Physical Properties

Atomic radii of second row d-metals (Period 5) are typically larger than in the first row (Period 4).

The third row (Period 6), are about the same as those in the second row (Period 5) and smaller than expected. This is due to the **lanthanide contraction** - the increasing nuclear charge coupled with the poor shielding ability of f-electrons.

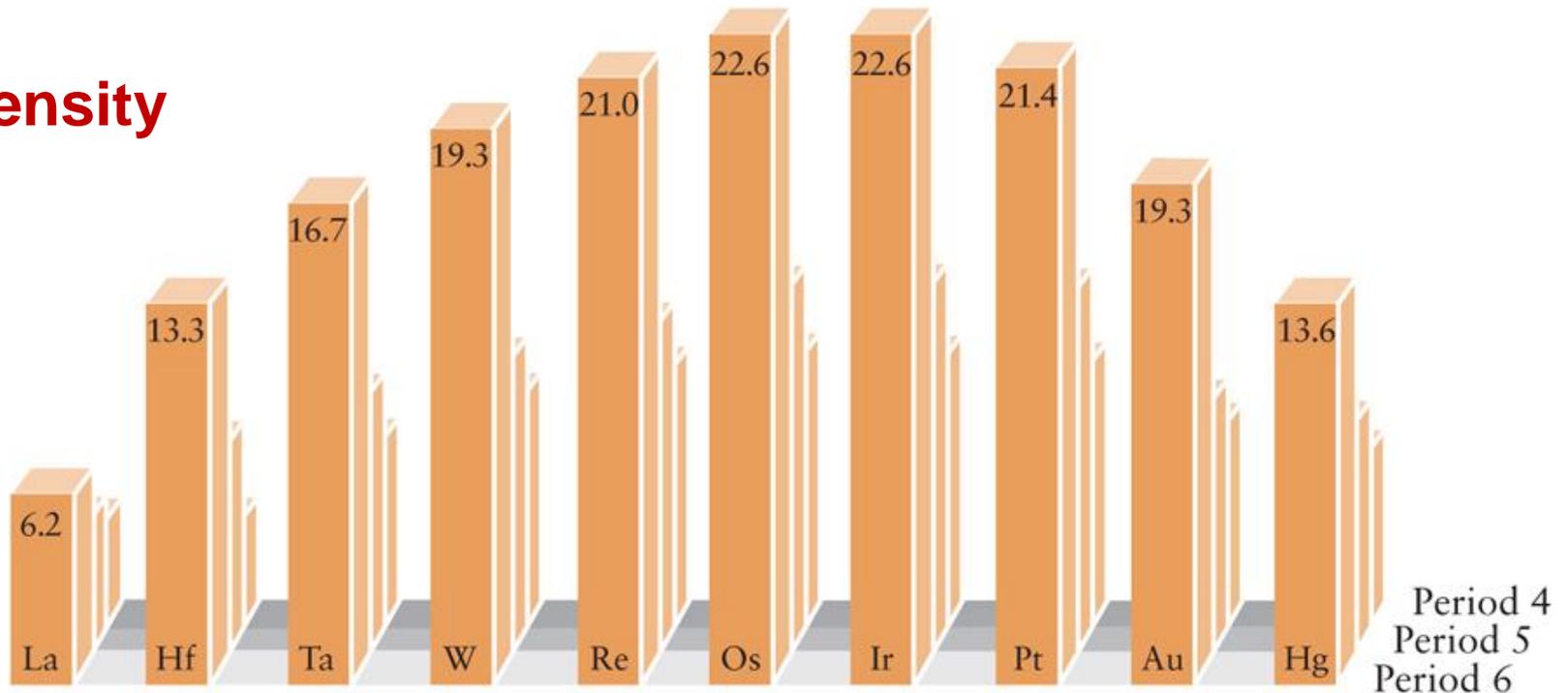
		Group									
		3	4	5	6	7	8	9	10	11	12
Period	4	Sc 161	Ti 145	V 132	Cr 125	Mn 137	Fe 124	Co 125	Ni 125	Cu 128	Zn 133
	5	Y 181	Zr 160	Nb 143	Mo 136	Tc 136	Ru 134	Rh 134	Pd 138	Ag 144	Cd 149
	6	La 188	Hf 156	Ta 143	W 137	Re 137	Os 135	Ir 136	Pt 138	Au 144	Hg 160

Physical Properties

Density: Iridium's volume is the same as rhodium, but Ir has twice the mass of Rh so iridium has twice the density.

Nobility (noble gas-like): of gold and platinum is due to their valence electrons being relatively close to the nucleus (held more tightly) and therefore unreactive.

Density



Chemical Properties

The d-block elements tend to lose their valence **s-electrons** first when forming compounds.

Most lose a **variable number of d-electrons** and exist in a variety of oxidation states.

Only Group 12 (zinc, cadmium, and mercury) lose their **single s-electron** and no d-electrons.

Chemical Properties

Most have **multiple oxidation state**.

1.) **Center elements** have the **widest range** of oxidation states.

2.) **Second and third** rows reach **higher** oxidation states.

Common.
Other Known.

8										
7					Common					
6			Common	Other Known	Other Known					
5			Other Known	Other Known	Other Known					
4		Other Known								
3	Other Known									
2		Other Known								
1			Other Known	Other Known		Other Known	Other Known	Other Known		
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

8					Other Known					
7					Other Known	Other Known				
6				Other Known	Other Known	Other Known				
5			Other Known	Other Known	Other Known	Other Known				
4		Other Known								
3	Other Known									
2		Other Known								
1		Other Known	Other Known					Other Known	Other Known	
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd

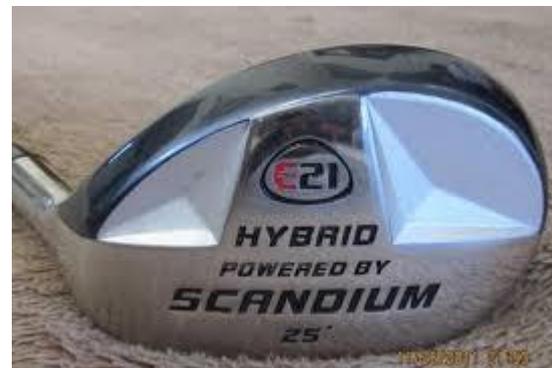
8					Other Known					
7					Other Known					
6				Other Known	Other Known	Other Known	Other Known			
5			Other Known							
4		Other Known								
3	Other Known		Other Known	Other Known						
2			Other Known							
1		Other Known	Other Known		Other Known	Other Known		Other Known	Other Known	
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Selected Elements: A Survey

Scandium, Sc, reacts in a similar to water as calcium.

The small, highly charged Sc^{3+} ion is strongly hydrated in water (like Al^{3+}), and the resulting $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$.

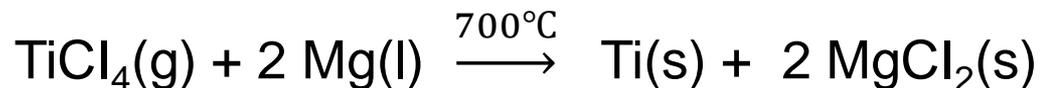
It is not thought to be essential to life.



Selected Elements: A Survey

Titanium, Ti, a light, strong metal, is less reactive than scandium because of its passivated oxide skin.

Titanium requires strong reducing agents for extraction from its ores:



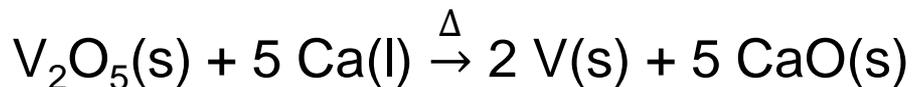
The most common oxidation state of titanium is +4, TiO_2 .

TiO_2 , is universally known as titanium dioxide, a brilliantly white, nontoxic white pigment in paints and paper.



Selected Elements: A Survey

Vanadium, V, a soft silver-gray metal is produced by reducing its oxide or chloride:



Vanadium is used to make tough steels for automobile and truck springs, but it is expensive to add the pure V to iron, instead, cheaper carbon is added.

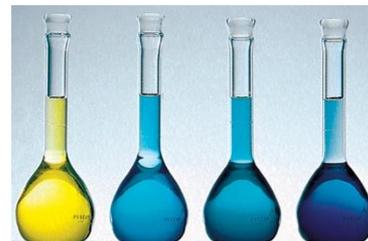


Steel



V_2O_5 is an orange-yellow solid used as a catalyst to manufacture sulfuric acid.

The ceramics industry uses the wide range of vanadium colors, including the blue of the vanadyl ion, VO^{2+} .



Selected Elements: A Survey

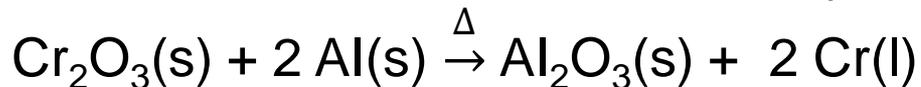
Chromium, Cr, is a bright, lustrous, corrosion-resistant metal used in stainless steel and for chromium plating.



The metal is obtained from the mineral chromite, FeCr_2O_4 , by reduction with carbon in an electric arc furnace:



Chromium metal is also reduced by aluminum in the **thermite process**:



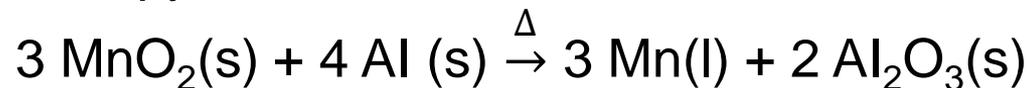
Selected Elements: A Survey

Manganese, Mn, is a gray metal that resembles iron, mainly used in alloys.

It is less resistant to corrosion than chromium due to a coating of a thin brown layer of oxide when exposed to air.

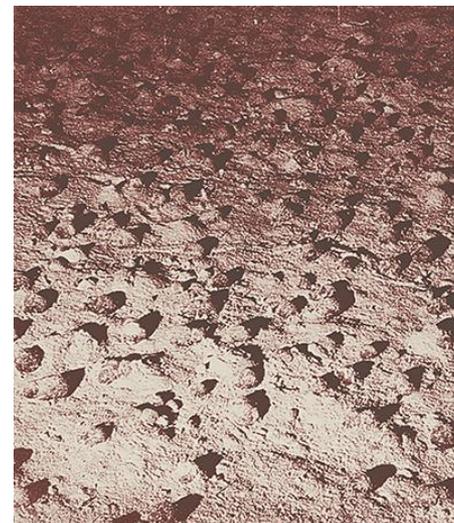
Manganese is also alloyed with aluminum to increase the stiffness of beverage cans, allowing them to be manufactured with thinner walls.

Manganese is obtained by a **thermite process** from pyrolusite:



Manganese nodules that litter the ocean floor are potentially a valuable source of the element.

Manganese (Group 7) has stable oxidation states of +2, but +4, +7, and +3 are common.



Selected Elements: A Survey

Iron, Fe, the most widely used of all the d-metals, is the most abundant d-element on Earth and the second most abundant metal in the Earth's crust (after aluminum).

Its ores are the oxides hematite, Fe_2O_3 , and magnetite, Fe_3O_4 , and the sulfide mineral pyrite, FeS_2 .

Iron is quite reactive and corrodes in moist air.



Like nickel, iron can form zero oxidation number compounds like iron pentacarbonyl, $\text{Fe}(\text{CO})_5$.

Healthy adult human body contains about 3 g of iron, mostly as hemoglobin.

About 1 mg is lost daily (in sweat, feces, and hair), and women lose about 20 mg in each menstrual cycle, iron must be ingested daily to maintain the balance.

Selected Elements: A Survey

Cobalt, Co, is a silver-gray metal and is used mainly for alloying with iron.

Alnico steel, an alloy of iron, nickel, cobalt, and aluminum, is used to make *permanent magnets* such as those in loudspeakers.

Cobalt steels are hard enough to be used as surgical steels, drill bits, and lathe tools.



The color of cobalt glass is due to a blue pigment.



Selected Elements: A Survey

Nickel, Ni, is also used in alloys. It is a hard, silver-white metal used mainly for the production of stainless steel or a copper-nickel alloy cupronickels.



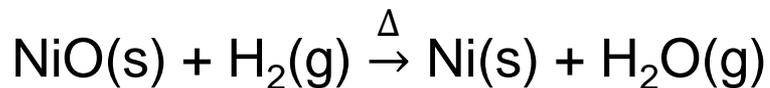
Nickel is also used in NiCad batteries.



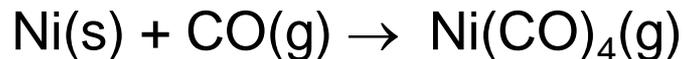
It is a catalyst for adding hydrogen to organic compounds, as in the hydrogenation of vegetable oils.

Selected Elements: A Survey

Nickel ore is first roasted (heated in air) in the **Mond process**:



Then exposed to carbon monoxide.



$\text{Ni(CO)}_4\text{(g)}$ is poisonous, boils at 43°C , so removed from other impurities. It is finally decomposed at 200°C back to the metal.



Groups 11 & 12

Group 11 contains coinage metals-copper, silver, and gold.

Group 12 contains zinc, cadmium, and mercury.

The low reactivity is partly due to the **poor shielding** of the d-electrons resulting in the nucleus exerting a tighter-grip on the outermost electrons.

Z	Name	Symbol	Valence electron configuration	Melting point (°C)	Boiling point (°C)	Density, (g·cm ⁻³)
29	copper	Cu	3d ¹⁰ 4s ¹	1083	2567	8.93
47	silver	Ag	4d ¹⁰ 5s ¹	962	2212	10.50
79	gold	Au	5d ¹⁰ 6s ²	1064	2807	19.28
30	zinc	Zn	3d ¹⁰ 4s ²	420	907	7.14
48	cadmium	Cd	4d ¹⁰ 5s ²	321	765	8.65
80	mercury	Hg	5d ¹⁰ 6s ²	-39	357	13.55

Groups 11 & 12

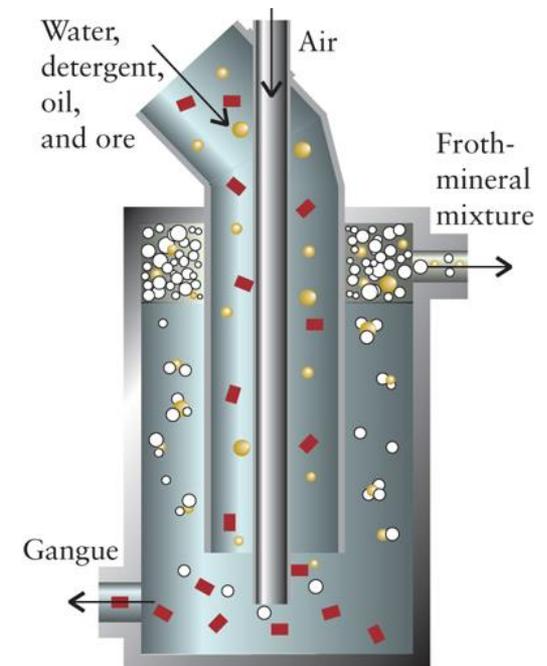
Copper, Cu, is unreactive enough for it to be found as the metal, but most is found as a **sulfide chalcopyrite**, CuFeS_2 .



CuFeS_2 is crushed and ground where excess rock is separated by froth flotation.

A powder is combined with oil, water, and detergents.

Air is blown through the mixture; the oil-coated sulfide mineral floats to the surface with the froth, and the unwanted copper-poor residue, which is called **gangue**, sinks to the bottom.



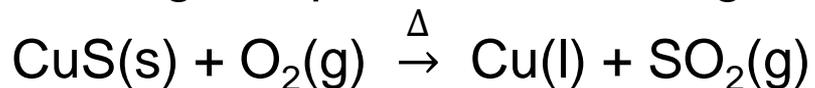
Groups 11 & 12

Extracting metals from ores is done by either *pyrometallurgical*, using high temperatures, or *hydrometallurgical*, enlisting aqueous methods. Copper uses both.

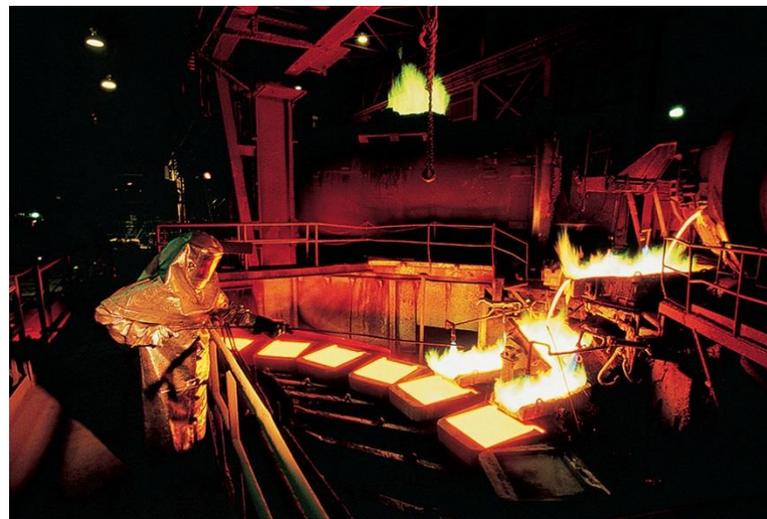
Pyrometallurgical extraction, is roasting:



The CuS is then smelted, reducing the metal ions by heating and a reducing agent such as carbon (in the form of coke). Sulfur is oxidized to SO₂ by blowing compressed air through the mixture of ore, limestone, and sand:



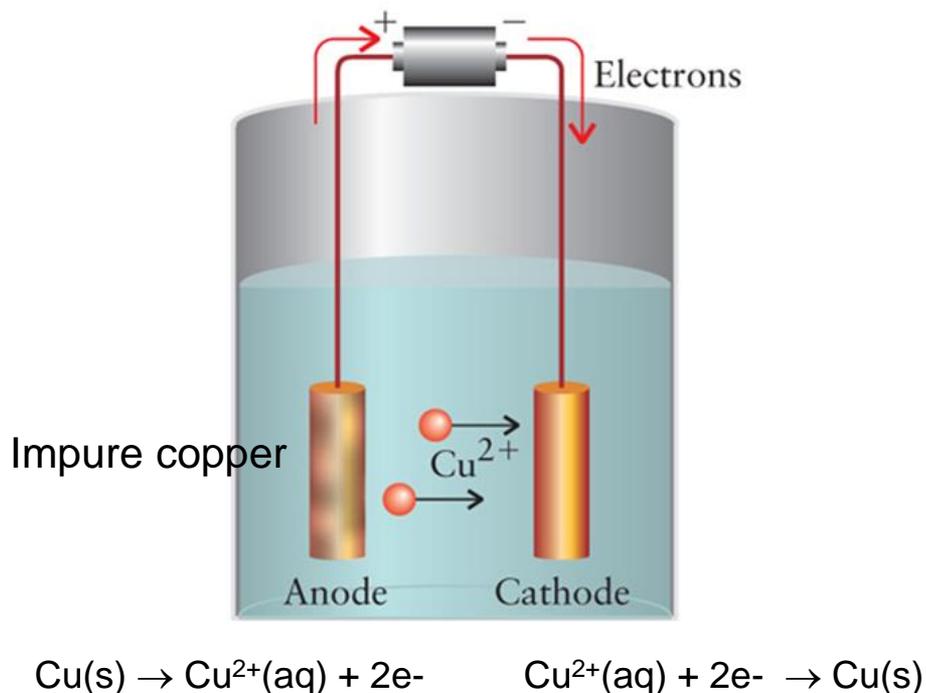
When liquid copper metal cools it forms **blister copper** the appearance of bubbles when the metal cools.



Groups 11 & 12

The impure copper from either process is refined electrolytically: it is made into anodes and plated onto cathodes of pure copper.

During the electrolysis of copper rare metals-most notably, platinum, silver, and gold-are obtained from the anode sludge ore sold to recover much of the cost of the electricity used in the electrolysis.



Groups 11 & 12

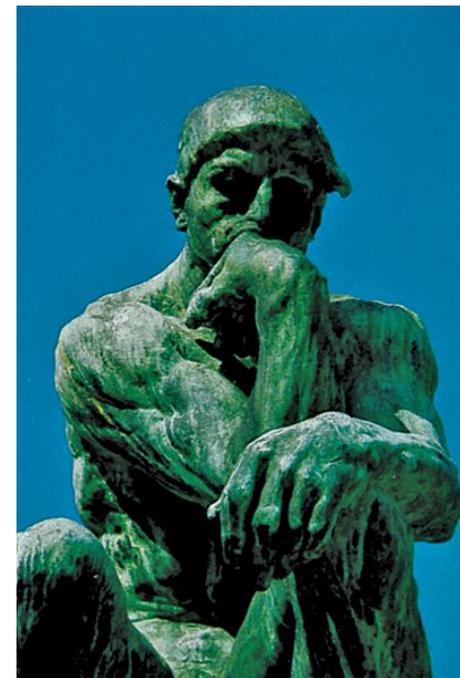
Copper alloys such as brass and bronze, are harder and more resistant to corrosion.



Copper corrodes in moist air in the presence of oxygen and carbon dioxide:



The pale green is called *basic copper carbonate* and is the green patina of copper and bronze objects.

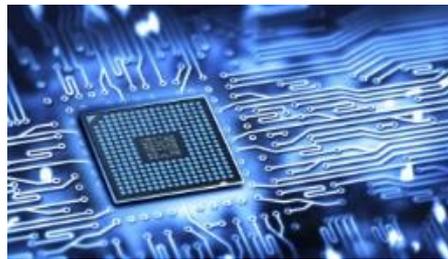


Groups 11 & 12

Silver, Ag, is rarely found as the metal, usually obtained as a byproduct of copper and lead refining.

Silver has a **positive standard potential**, and so it does not react with acids to make hydrogen gas.

Instead Ag reacts with sulfur to form the familiar black tarnish Ag_2S .



Groups 11 & 12

Gold, Au, is so inert it is found in nature as the metal. Pure gold is classified as 24-carat gold.

Its alloys with silver and copper, to harden it.

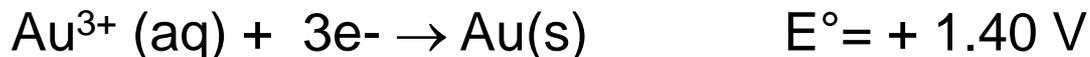
Gold is a highly malleable metal, and 1 g of gold can be worked into a leaf covering an area of about 1 m² or pulled out into a wire more than 2 km long.

Gold leaf provides a valuable decorative protection, such as that on dishes and books.



Groups 11 & 12

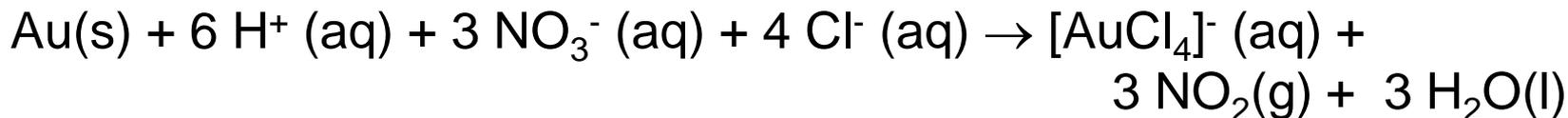
Gold is **too noble** to react even with strong oxidizing agents such as nitric acid. Both the gold couples:



lie above H^+/H_2 and NO_3^- , H^+/NO , H_2O :



Gold does react with **aqua regia**, concentrated **HNO_3/HCl** forming the complex ion $[\text{AuCl}_4]^-$:

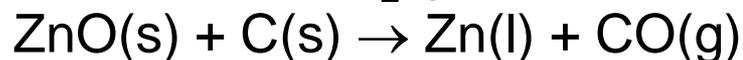
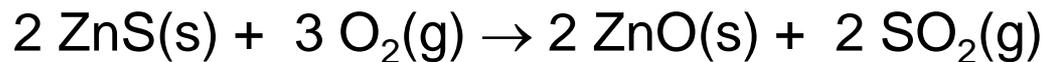


Groups 11 & 12

Zinc, is found mainly as its sulfide, ZnS (sphalerite).



The metal is isolated by a froth flotation, and the metal is extracted by roasting and then smelting with coke:

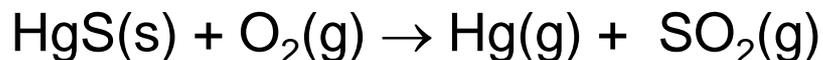


Zinc is used mainly for galvanizing iron or it is combined with Cu to make brass.



Groups 11 & 12

Mercury, Hg, occurs mainly as Hg in the mineral cinnabar (HgS) and separated by froth flotation and then roasting in air:



The volatile metal is separated by distillation and condensed.

It is the only metal liquid at room temperature (gallium and cesium are liquids on warm days), its melting point is -39°C and it boils at 357°C .

Mercury has oxidation numbers +1 or +2. The most common is the oxidation number +1.

Organic mercury compounds, are acutely poisonous.

Mercury vapor is an insidious poison because its effect is cumulative, causing neurological problems and hearing loss, and other ailments.

Coordination Compounds

Many d-block elements form colored solutions in water.

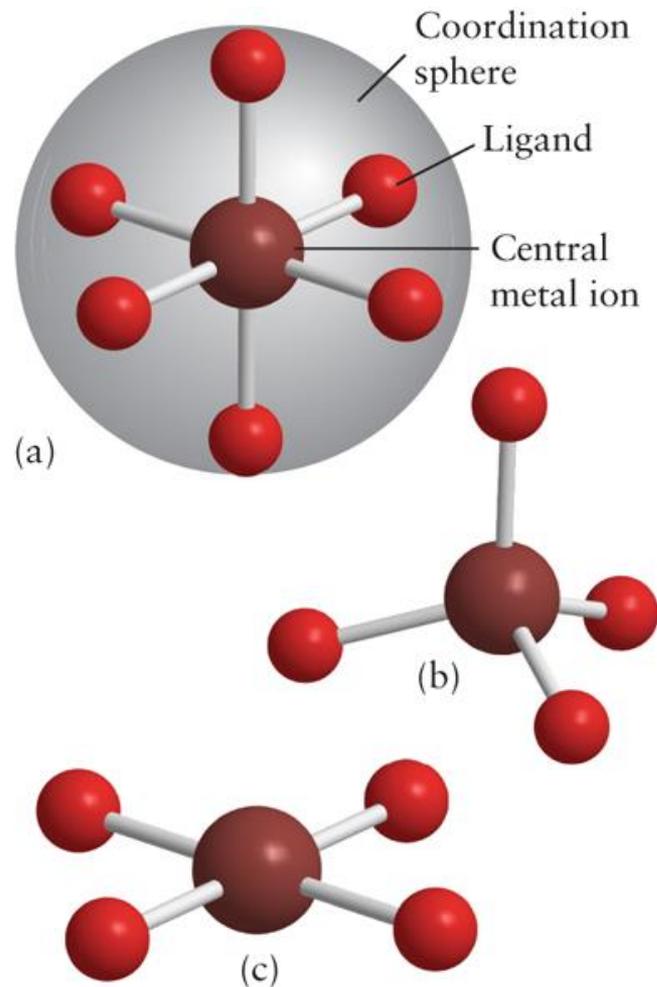
Solid copper(II) chloride is **brown** but in water it is **blue**.

Solid copper(II) bromide is **black** but in water it is **blue**.

The water is a complex, coordinated to the metal in a **Lewis acid Lewis base** interaction called a ***coordination compound***.

Coordination Compounds

Ligands are either **molecules or ions** coordinating to d-metal ions in a **Lewis acids Lewis bases interaction**.



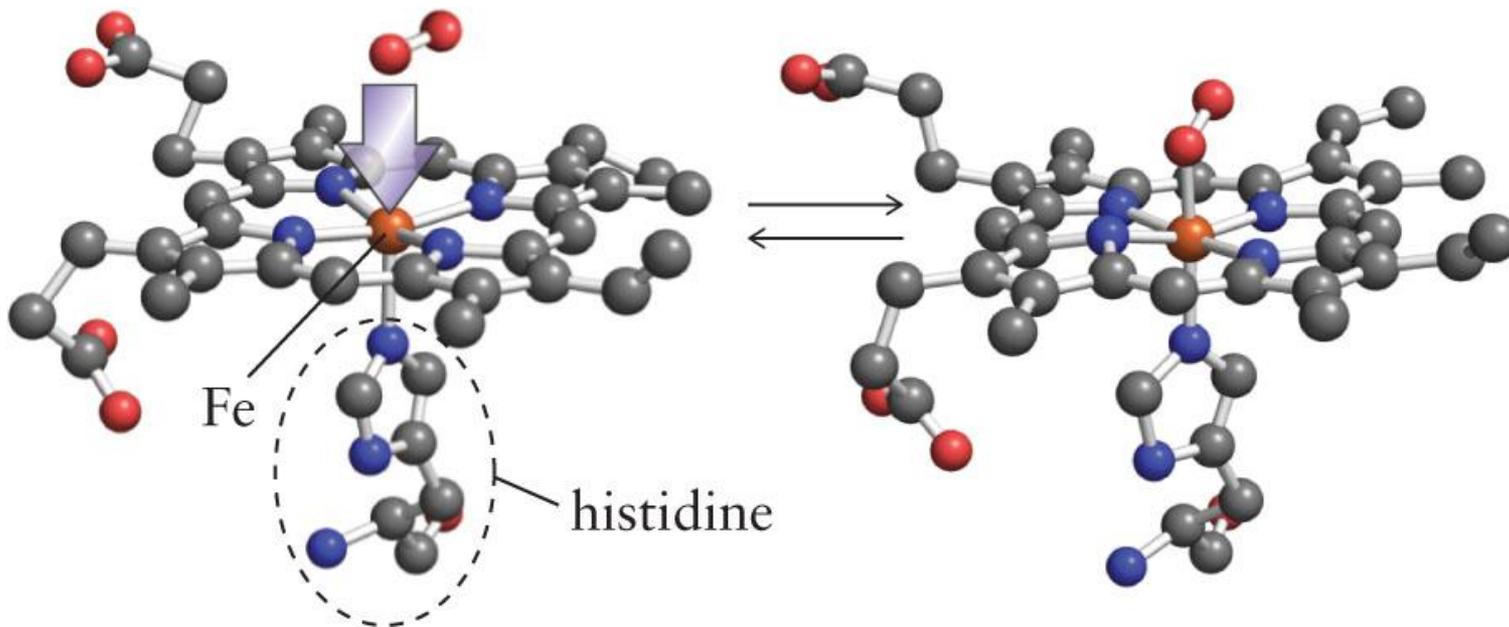
Amino acids chains, and polymers, with at least one metal are often enzymes, and in our cells are called **metalloproteins**.

Coordination Compounds

Hemoglobin, has an iron(II) at the center of a heme group.

4 nitrogen atoms hold a iron (II) in a square planer geometry, where oxygen is the 5th ligand.

Oxygen is absorbed or deabsorbed depending on the partial pressure of oxygen in the region of the heme.



Coordination Compounds

Zinc a master hormone- in enzymes, it plays a role in metabolism, gene expression, digestion of food, storage of insulin, and the building of collagen. In our bodies zinc and iron have the same concentration, and as we age zinc declines.

Chromium(III) plays a role in the regulation of glucose metabolism.

Copper(I) an essential nutrient for healthy cells and is the only biologically available Lewis acid with a + 1 charge.

Coordination Complexes

Ligands are Lewis bases attached to d-metal ions.

Ligand means to bind. They can be ionic or molecular.

Cyanide is ionic $[\text{Fe}(\text{CN})_6]^{4-}$.

Carbon monoxide is molecular $\text{Ni}(\text{CO})_4$.

Ligands coordinate to the metal center to form a complex.

In a complex formula, ligands attach directly to the metal so we enclose them in a [], **except for neutral complexes** with nickel above.

Coordination Complexes

Coordination number are the number of ligands, *directly attached* to the metal.

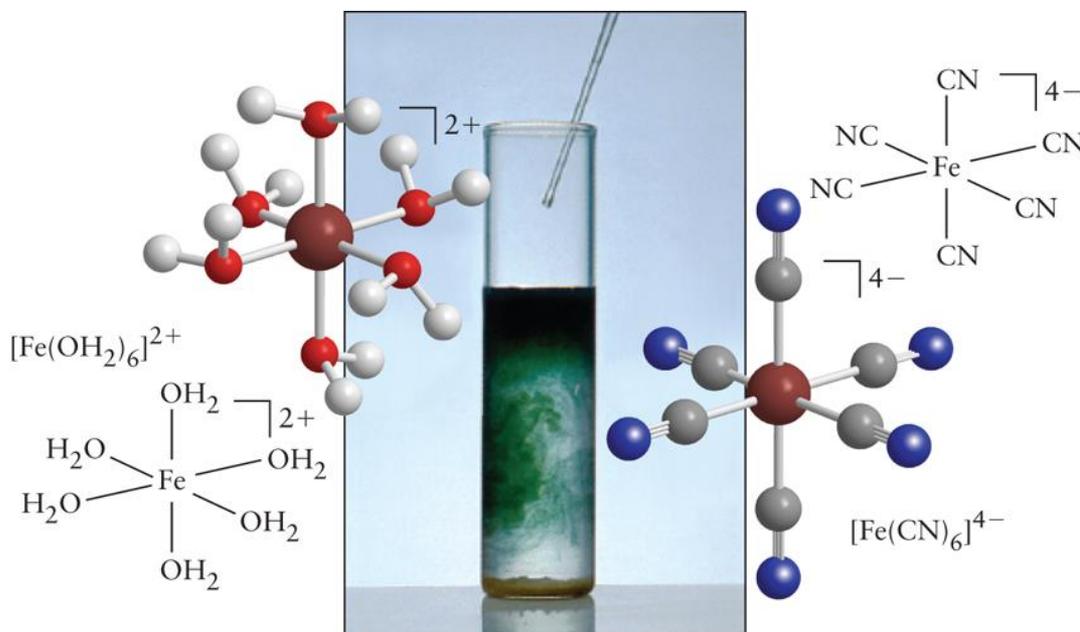
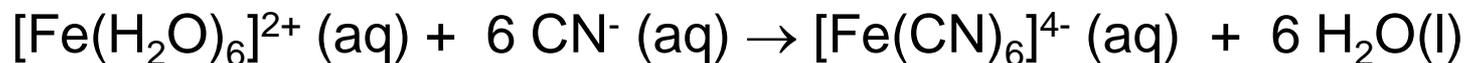
$[\text{Fe}(\text{CN})_6]^{4-}$ has a coordination number of 6 and $\text{Ni}(\text{CO})_4$ has a coordination number of 4.

Aqueous solutions of d-metal ions are usually solutions of their H_2O complexes: Fe^{2+} (aq), for instance, is more accurately $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

Water is a Lewis base, it forms complexes with most d-block ions when they dissolve in it.

Coordination Complexes

Many complexes are prepared simply by mixing aqueous solutions of a d-metal ion with the appropriate Lewis base (*spectator ions* are not written):



Typically **substitution reactions**, a Lewis base replacing another Lewis base. Often, water drives out the more weakly bound ligand, like Cl^- , attached to the metal.

Coordination Complexes

Coordination compound names can be awesomely long.

Chemists avoid problems by using the **chemical formula** rather than the name itself.

$[\text{FeCl}(\text{H}_2\text{O})_5]^+$ is simply pentaquachloroiron(II) ion.

Formula*

Name

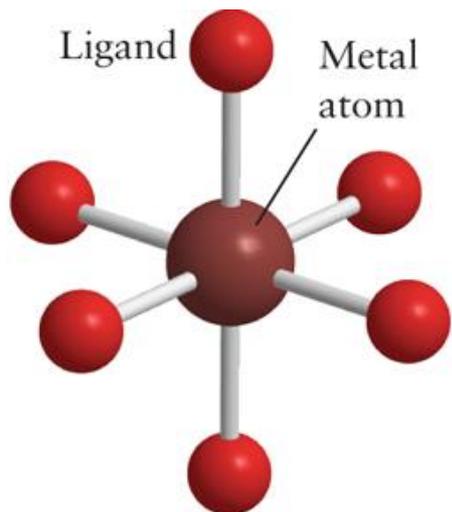
Neutral ligands

OH_2	aqua
NH_3	ammine
NO	nitrosyl
CO	carbonyl
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$	ethylenediamine (en) [†]
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$	diethylenetriamine (dien) [‡]

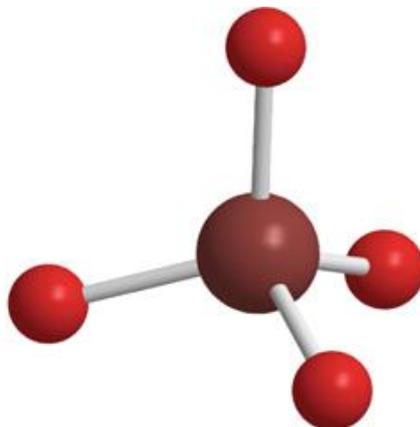
The Shape of Complexes

Most common complexes have 6 as a coordination number and are called **octahedral complexes**.

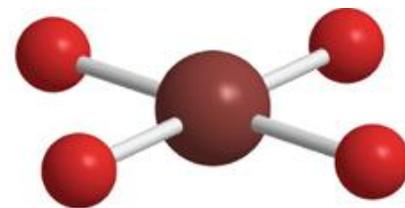
Tetrahedral complex, the four ligands are found at the vertices of a tetrahedron. An alternative is a **square planar complex** seen in d^8 electron configurations for Pt^{2+} and Au^{3+} .



1 An octahedral complex



2 A tetrahedral complex



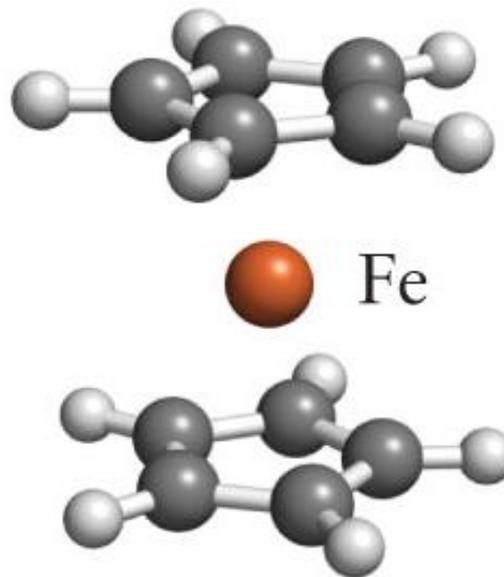
3 A square-planar complex

The Shape of Complexes

An interesting d-metal compound with 10 links between the ligands and the central metal ion is **ferrocene**, dicyclopentadienyliron(0), $[\text{Fe}(\text{C}_5\text{H}_5)]$.

Ferrocene is an aptly named a "sandwich compound," with the two planar cyclopentadienyl ligands the "bread" and the metal atom the "filling." The formal name for a sandwich compound is a **metallocene**.

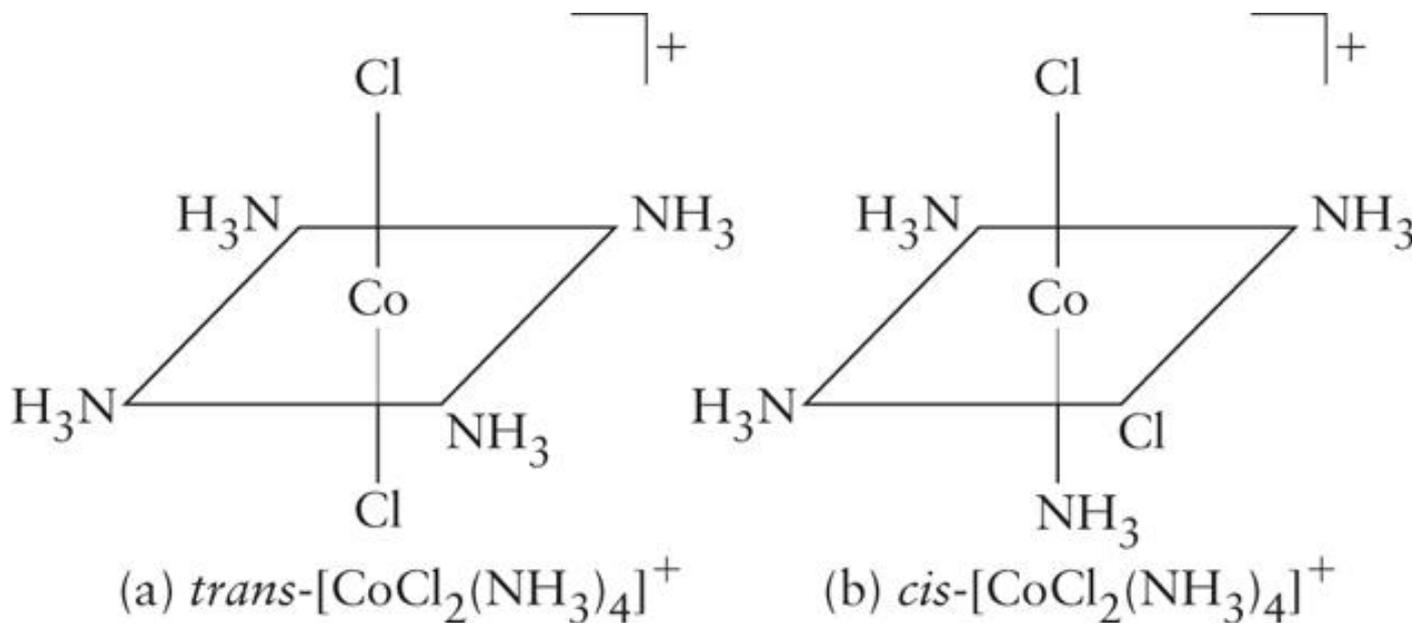
The rings rapidly spin, as if on an axis's, at room temperature.



Isomers

Many complexes exist as **isomers**, the *same compound*, except the atoms are arranged differently.

Cis- and trans- isomers differ by the location of the Cl⁻. These are distinct species with **different** physical and chemical properties.



Trans: Across

Cis: same side

Isomers

Two major classes of isomers are:

1. **Structural isomers**, atoms connect to different partners;
2. **Stereoisomers**, the atoms arranged differently in space.

Structural isomers are subdivided into:

- a) ionization,
- b) hydrate,
- c) linkage, and
- d) coordination isomers.

Stereoisomers are subdivided into:

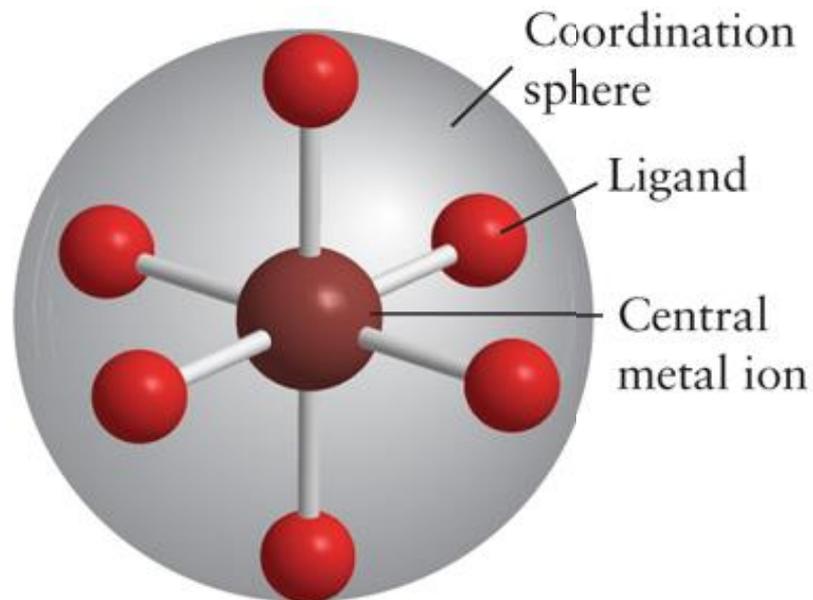
- a) Geometric
- b) Optical

Isomers

(a) Ionization isomers is an exchange of a ligand, anion or a neutral molecule, outside the coordination sphere.

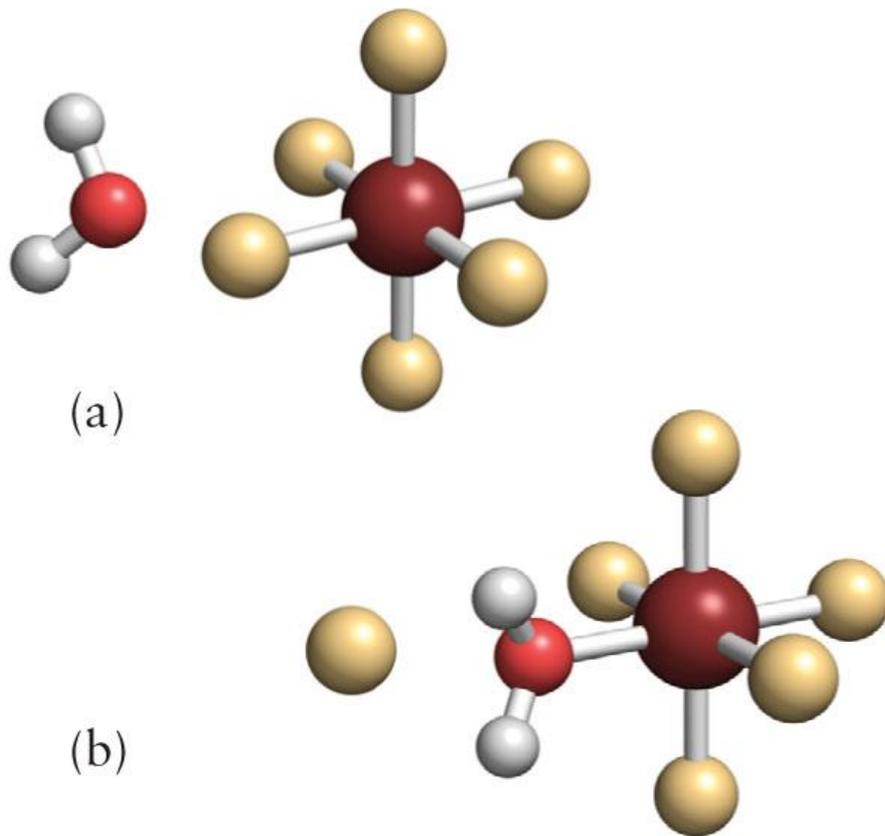


The Br^- ion ligand exchanges for the SO_4 inside and outside the coordination sphere.



Isomers

(b) Hydrate isomers differ by the exchange of an H_2O molecule with another ligand in the coordination sphere.

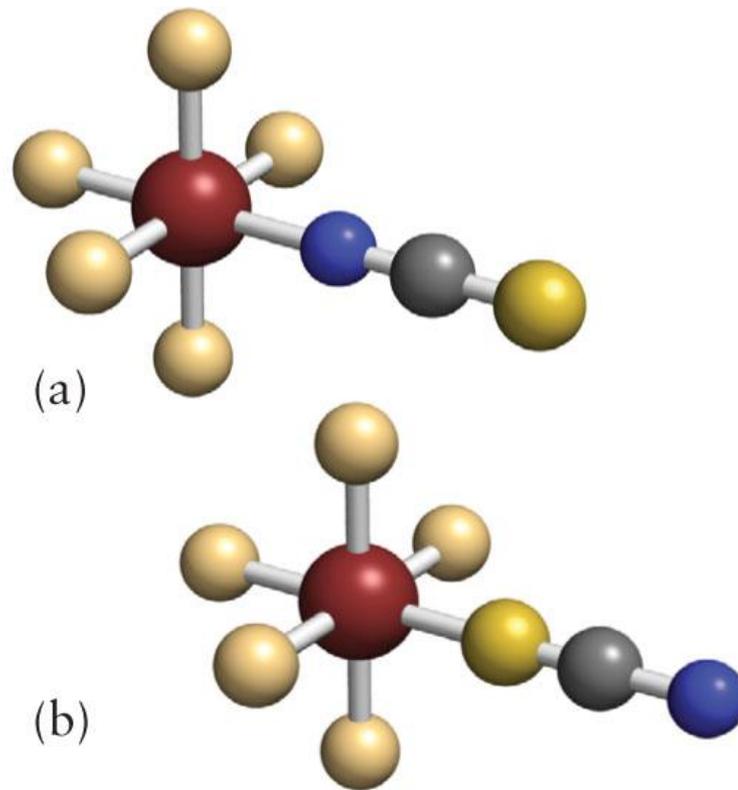


Isomers

(c) Linkage isomers differ in the ligand attachment to the metal ion.

Common linkage isomerism are SCN^- versus NCS^- , NO_2^- versus ONO^- , and CN^- versus NC^- , referred to as ambidentate ligands.

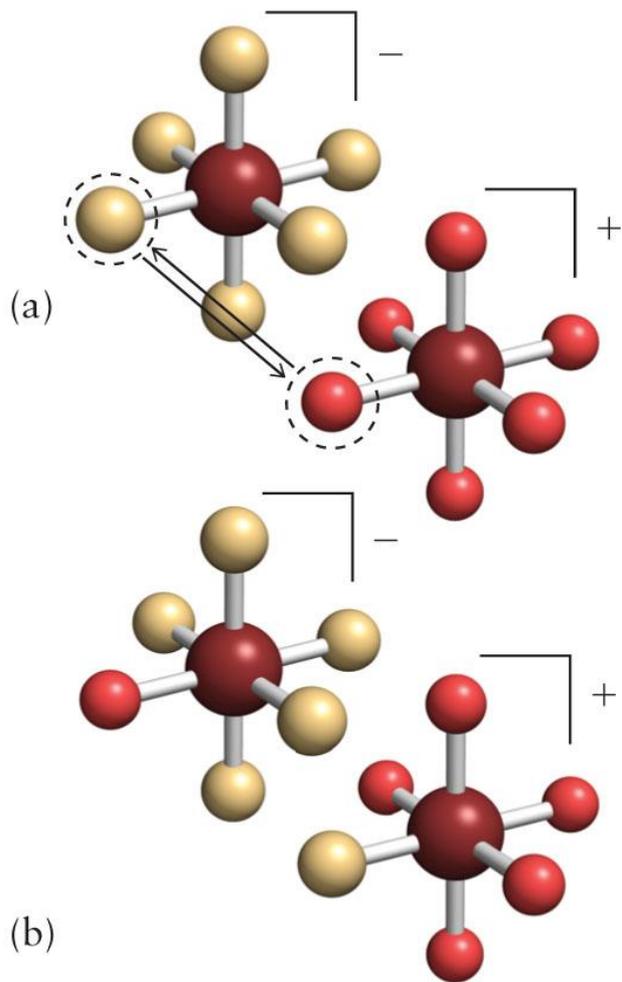
Write the attaching atom first,
 NO_2^- can form:



Isomers

(d) Coordination isomers differ by the exchange of one or more ligands between a cationic complex and an anionic complex.

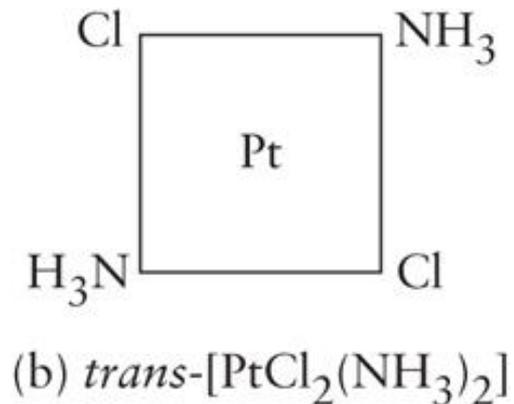
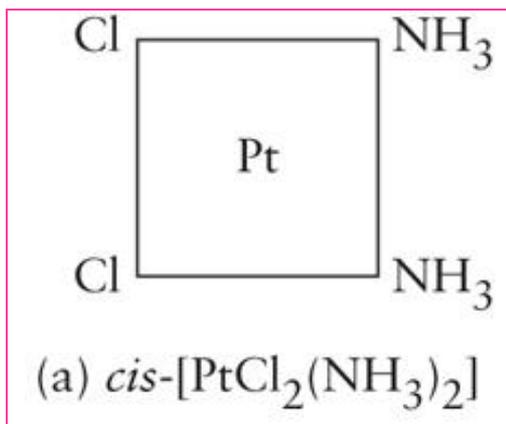
$[\text{Cr}(\text{NH}_3)_6][\text{Fe}(\text{CN})_6]$ and $[\text{Fe}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ are coordination isomers.



Isomers

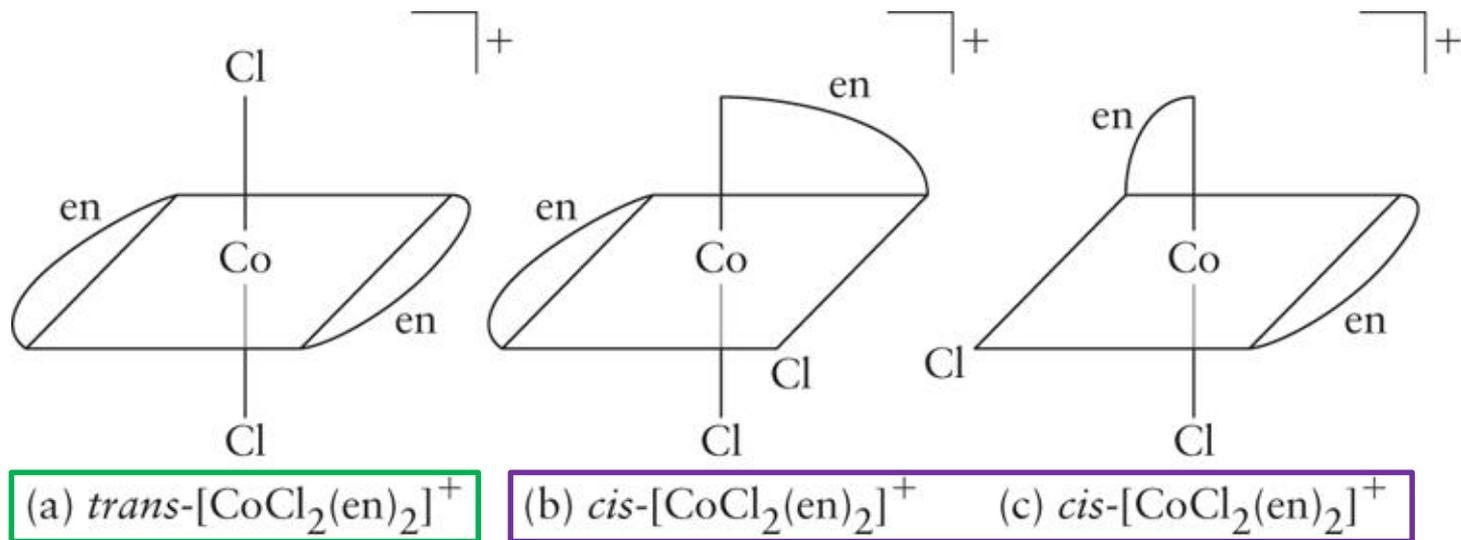
Stereoisomers differ by the **spatial arrangement** of the ligands: two different types exist **geometrical** and **optical**.

Geometrical isomers occurs for square planar and octahedral complexes but **not** for *tetrahedral* complexes. Chemical and physiological properties differ: *cis*-[PtCl₂(NH₃)₂] is used for chemotherapy not the *trans*-.



Isomers

Optical isomers are nonsuperimposable mirror images of each other. Both geometrical and optical isomerism can occur in an octahedral complex, as in $[\text{CoCl}_2(\text{en})_2]^+$:



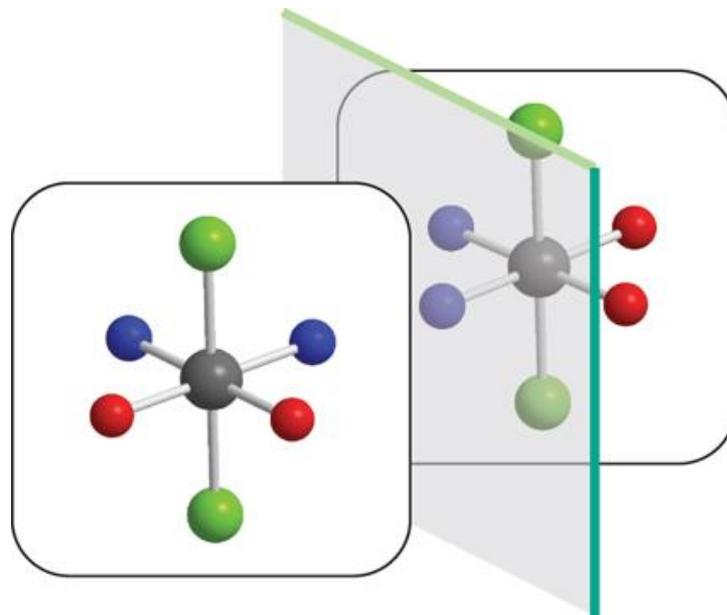
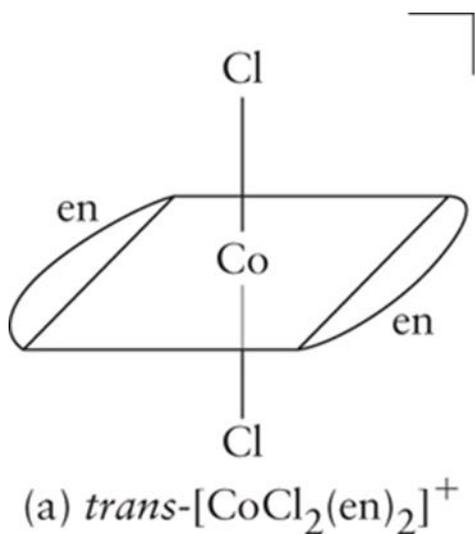
The trans is green, and the other two cis are a special case of optical isomers, called chiral (enantiomers), both are violet.

Isomers

Trans-isomer have ligands on opposite sides.

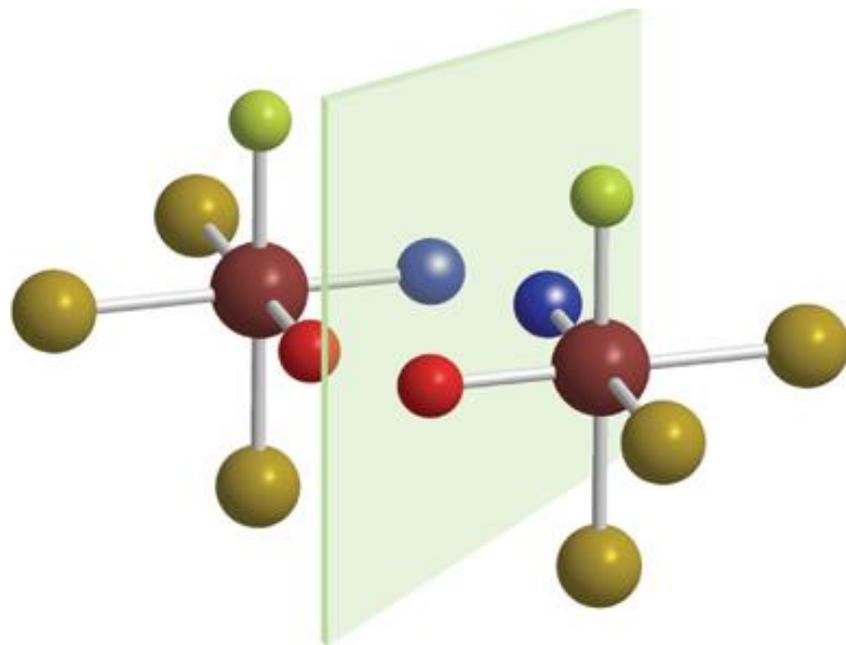
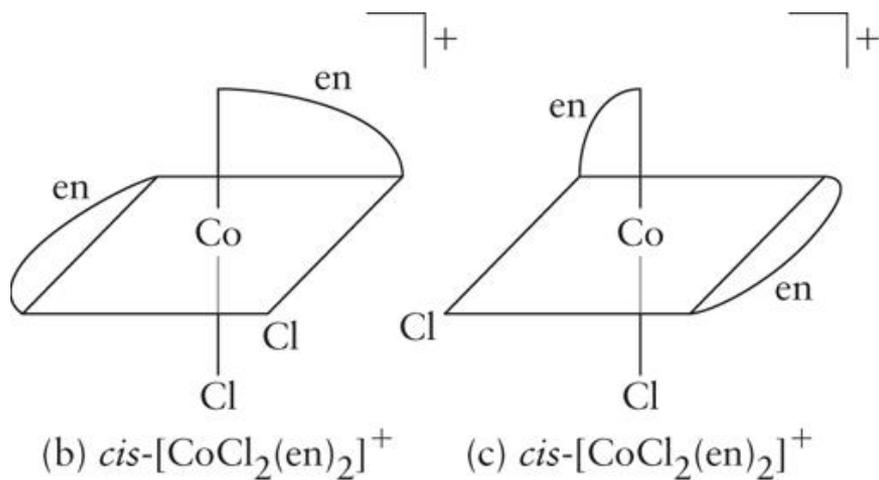
The trans isomer is **superimposable** on its mirror image so is **achiral**.

Rotating the images, in any direction, produces the same complex.

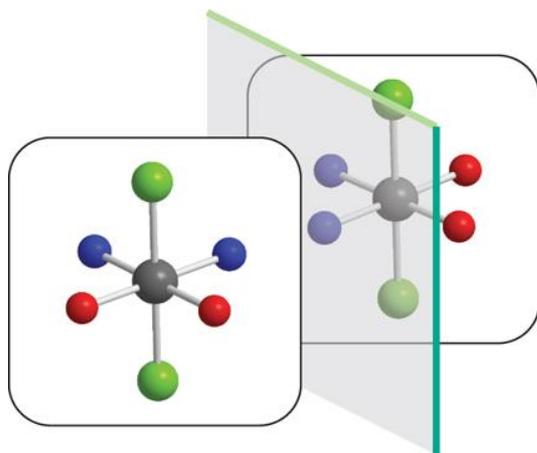
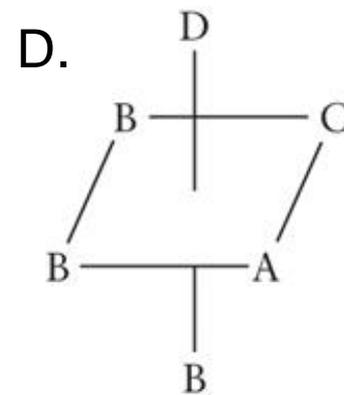
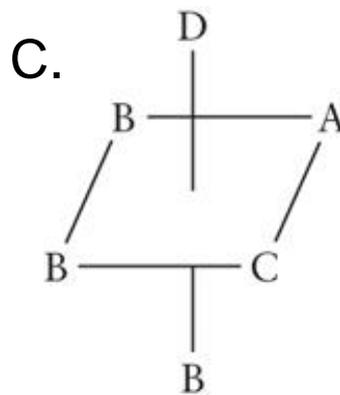
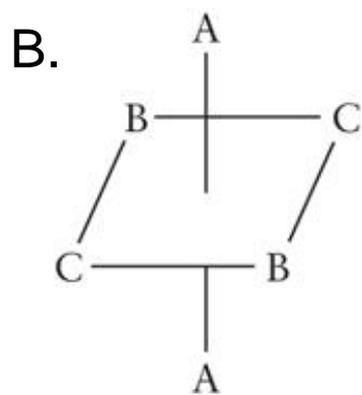
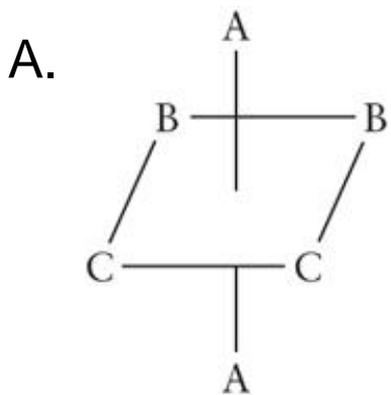


Isomers

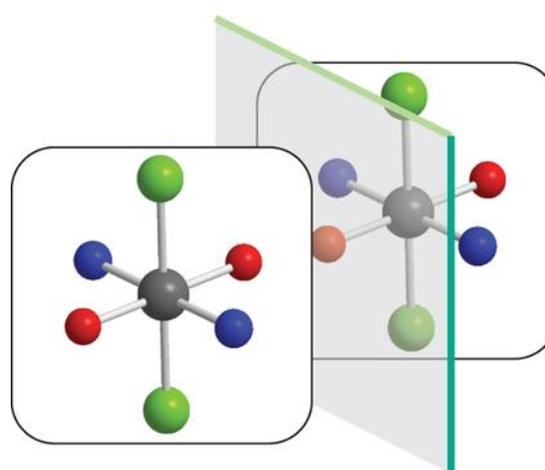
If a **chiral complex** has a mirror image, that is **non-superimposable** than these are a **pair of enantiomers**. Enantiomers have **wildly different chemical properties** but they have the **same physical property** except one, they rotate light so are said to be optically active.



Example 1: Which of the following complexes are chiral, and which form enantiomeric pairs?

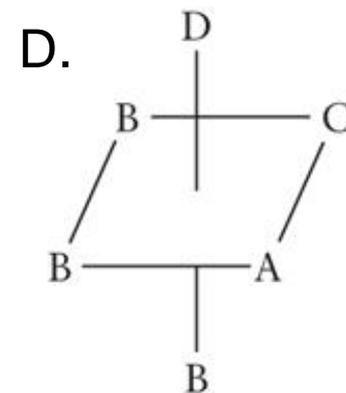
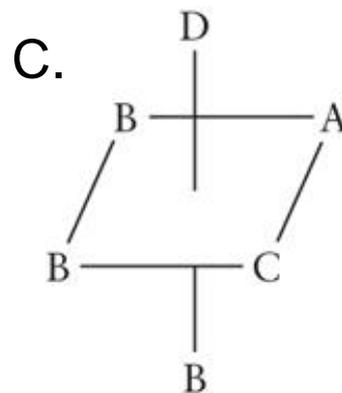
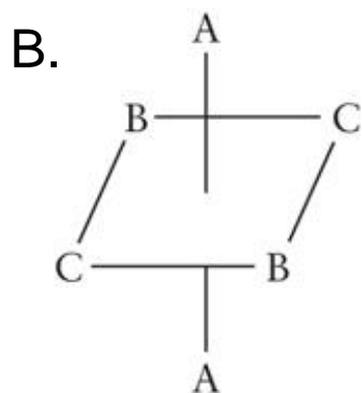
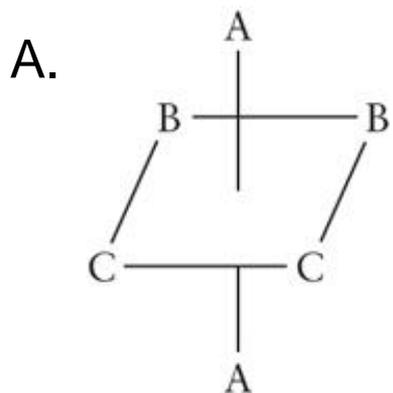


A. Not chiral

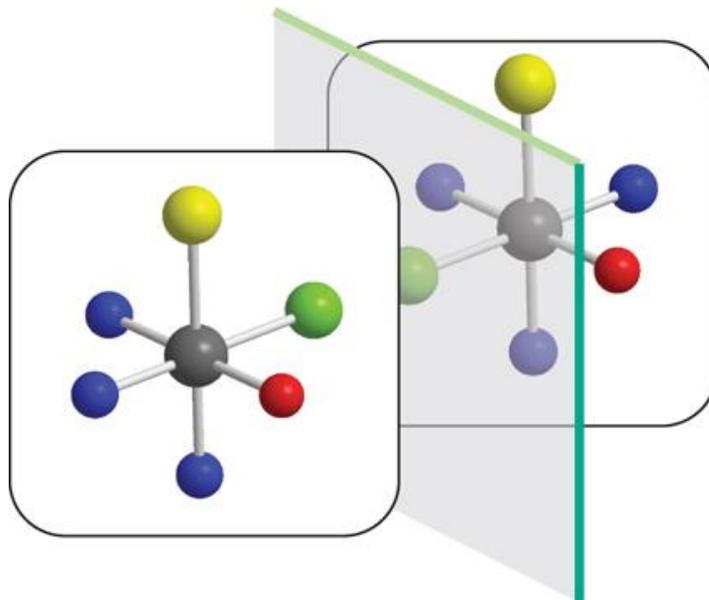


B. Not chiral

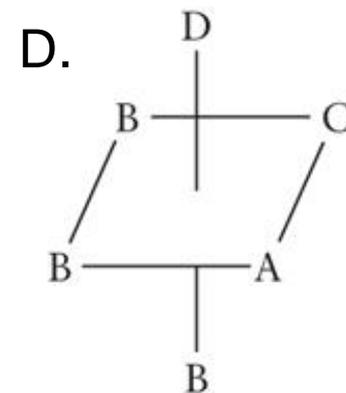
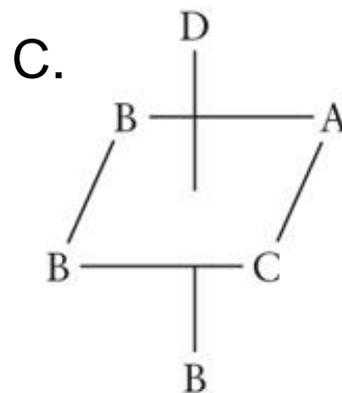
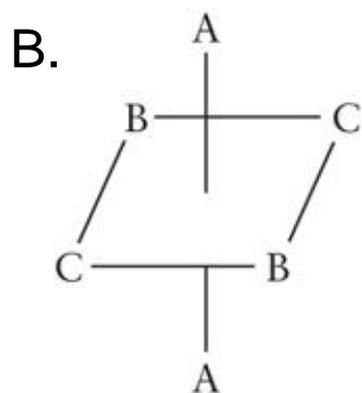
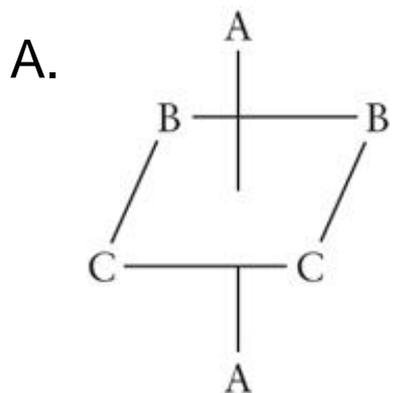
Example 1: Which of the following complexes are chiral, and which form enantiomeric pairs?



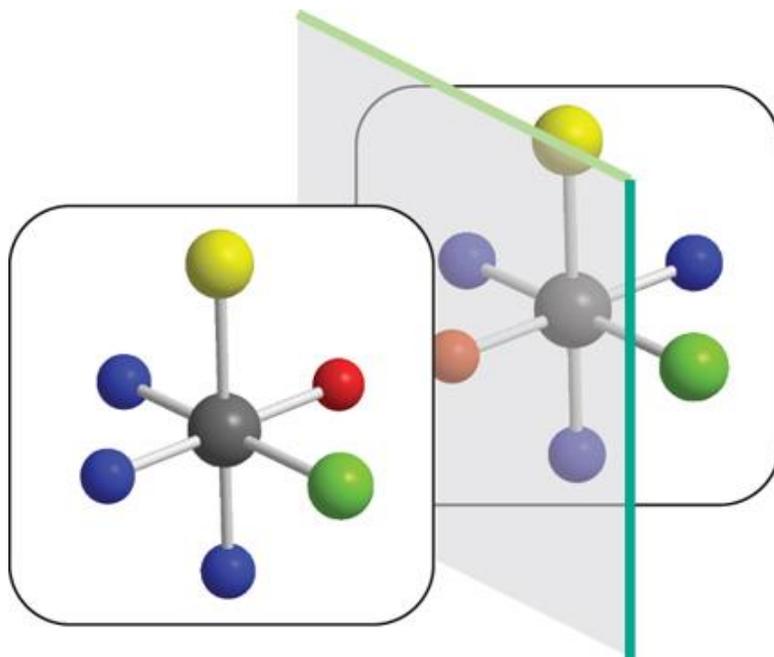
C. chiral



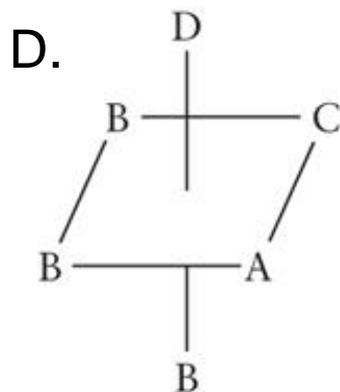
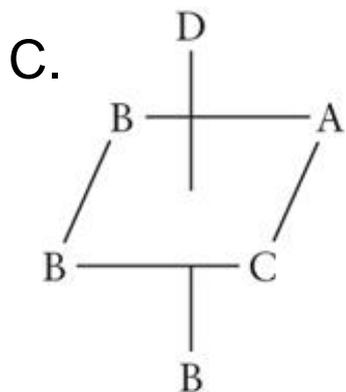
Example 1: Which of the following complexes are chiral, and which form enantiomeric pairs?



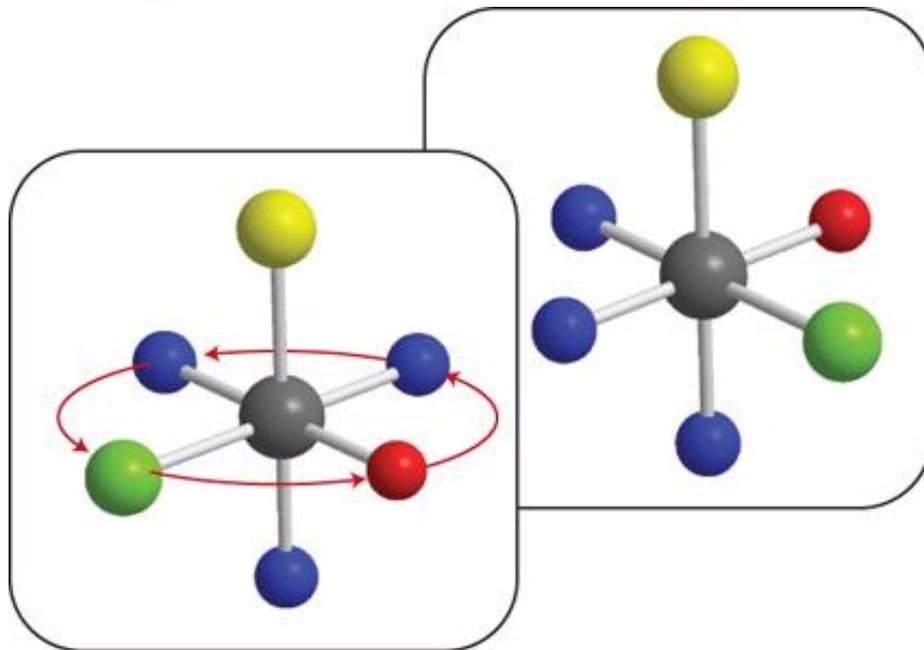
D. chiral



Example 1: Which of the following complexes are chiral, and which form enantiomeric pairs?



(c) and (d) are a pair of **enantiomers**, no matter how you rotate them, the molecules are different.



How do we detect optical activity

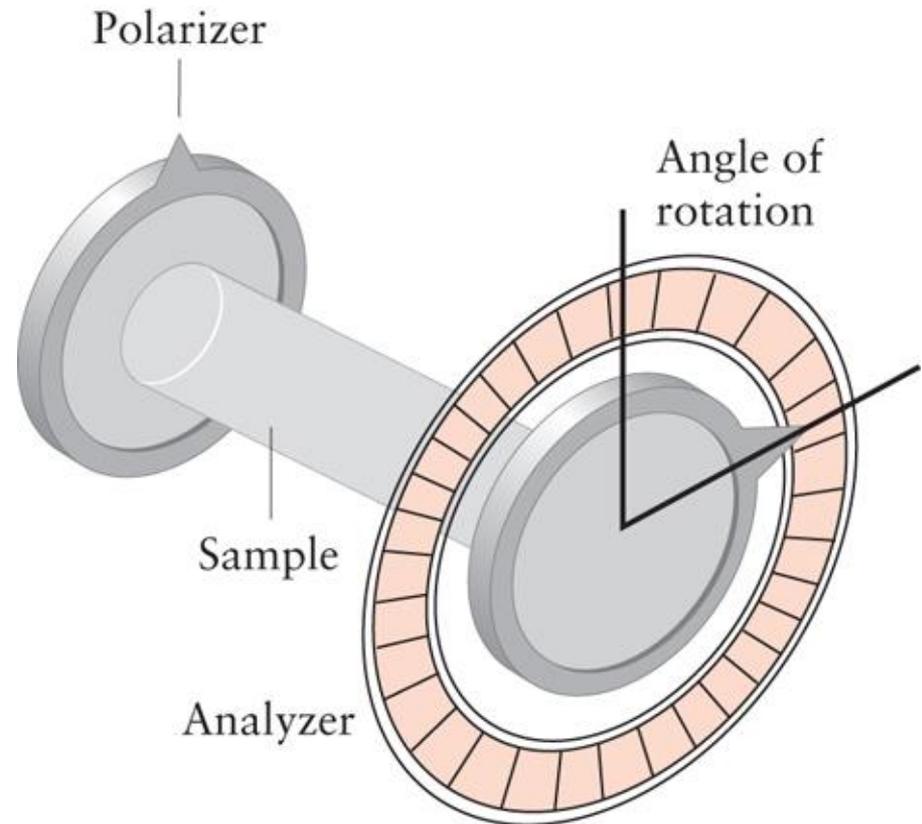
Light polarizers rotate the electric field into a single plane.

Optically active, **chiral complex**,
rotate the plane polarized light.

When light emerges, the angle of the newly rotated light is measured from its original angle.

A **achiral** compound **will not rotate** light.

This technique is called polarimetry.

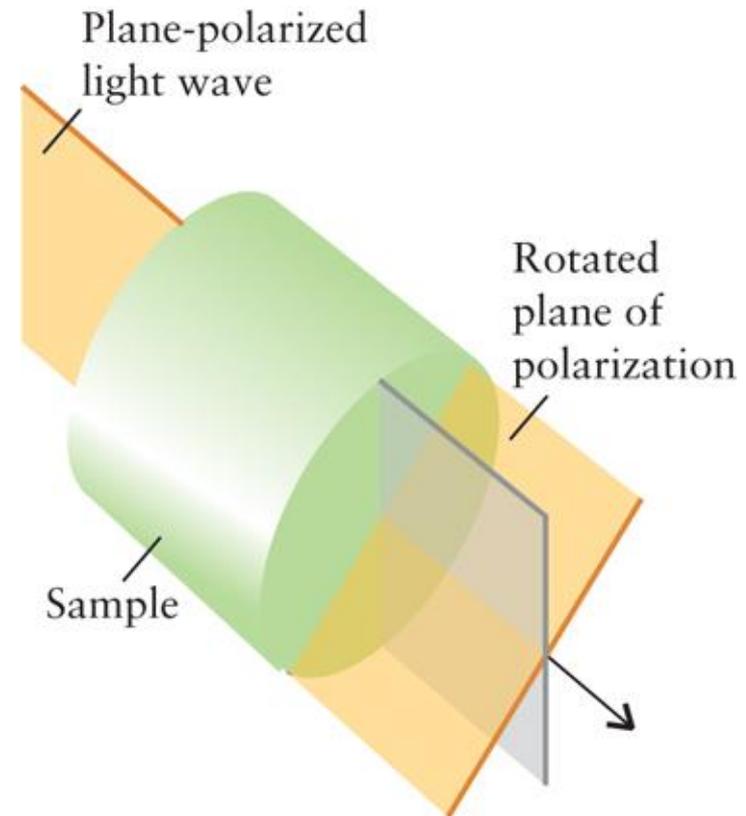


How do we detect optical activity

A **50:50 mixture** of a mixture of enantiomers will not rotate light (**racemic mixture**).

Some sample rotate light left, the other right. So if one enantiomer rotates light left, the other will rotate it right.

If the mixture changes to 25:75 then the angle is measurable.

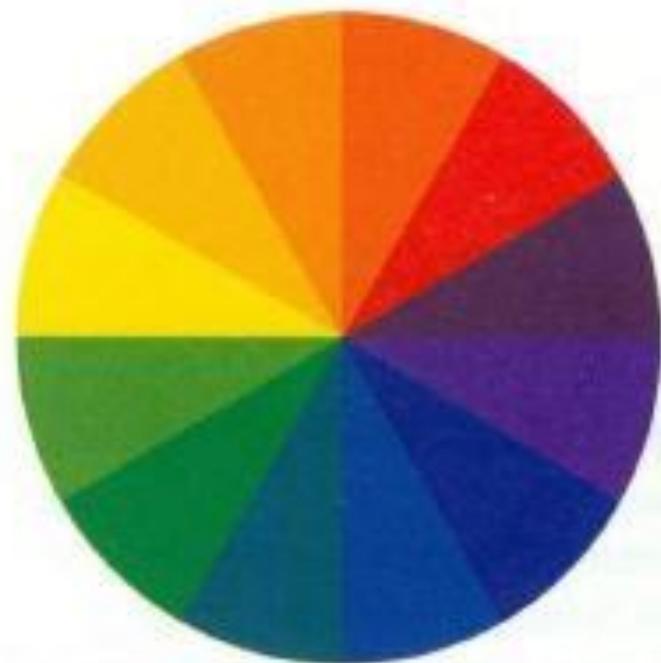


The Color of Complexes

White light is a mixture of all wavelengths of electromagnetic radiation from about 400 nm (violet) to about 700 nm (red).

If we **remove** one of the colors, the light will no longer be white.

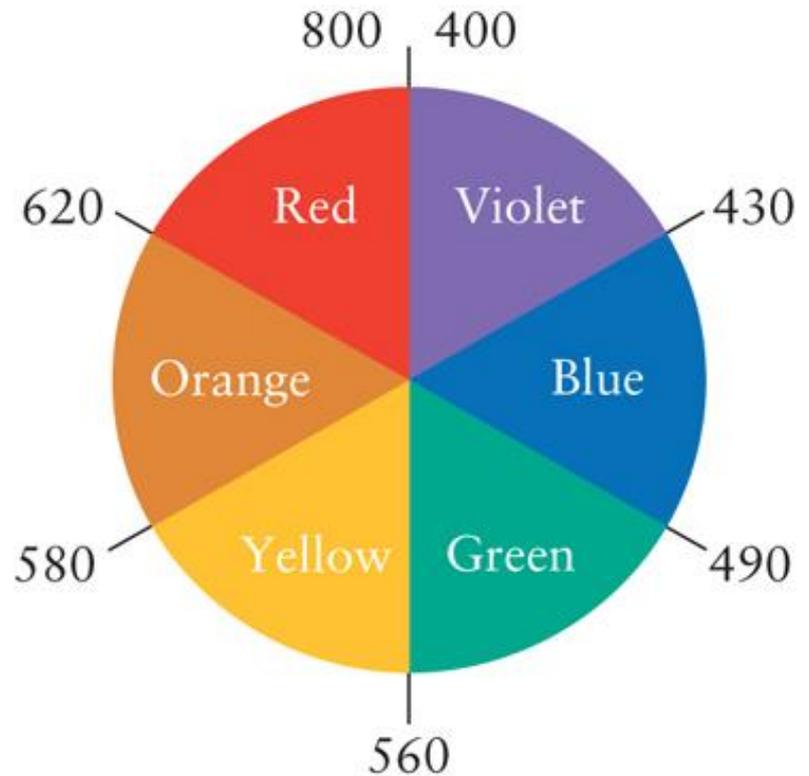
Colour	Wavelength range/nm
red	630–700
orange	590–630
yellow	560–590
green	490–560
blue	450–490
violet	400–450



The Color of Complexes

If we remove red light from white light, then the light that remains appears green. Conversely, removing green appears as red light.

We say that red and green are each other's complementary color-each is the color that white light appears when the other is removed



The Color of Complexes

If we know the wavelength (and therefore the color) of the light that a substance absorbs, then we can predict the color of the substance by noting the complementary color on the color wheel. Because $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs 570-nm light, which is yellow light, the complex looks violet.

