Coordination Compounds

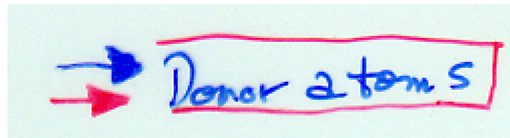
Definitions

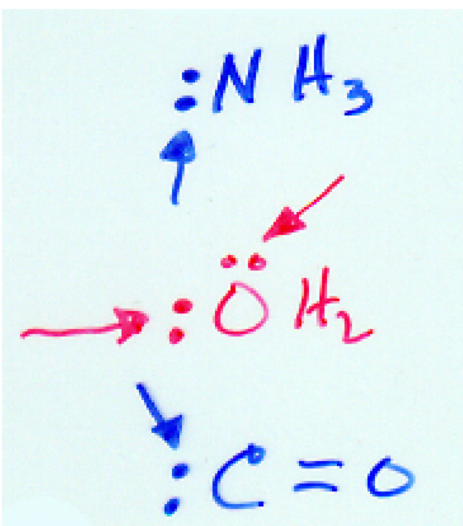
- Ligand: a Lewis base in a coordination compound
- Chelate: a ligand that utilizes 2 or more donor atoms in bonding to metals
- Coordination compound/Complex: a compound containing coordinate covalent bonds
- Coordinate covalent bond: the “Oral Roberts’ bond”

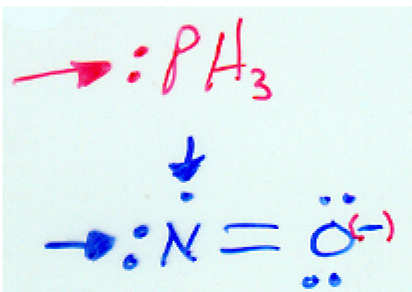
Cont'd

- Coordination number: the number of donor atoms coordinated to a metal
- Isomer: different substances with the same chemical formulas
- Polydentate: describes ligands with more than one donor atom
- Effective atomic number:
- The total number of electrons in the orbitals of the central metal ion after coordination occurs

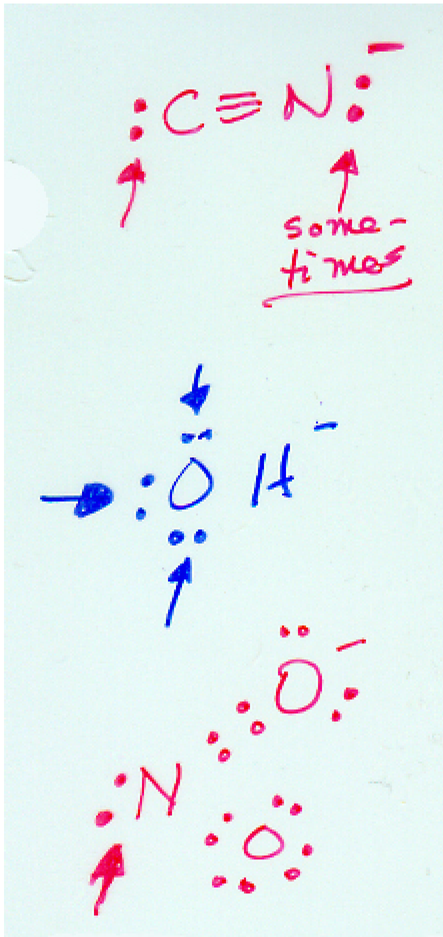
Simple Ligands



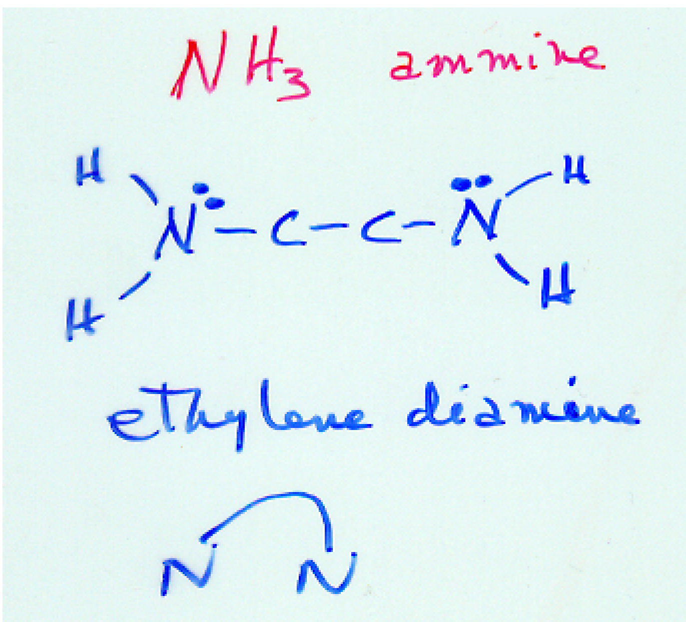
Molecule	Name	Ligand Name
	Ammonia	Ammine
	Water	Aqua
	Carbon monoxide	Carbonyl

<table>
<tr><th>Molecule</th><th>Name</th><th>Ligand Name</th></tr>
<tr><td rowspan="2">
</td><td>Phosphine</td><td>Phosphine</td></tr>
<tr><td>Nitrogen oxide</td><td>Nitrosyl</td></tr>
</table>

Molecule	Name	Ligand Name
	Chloride	Chloro
	Fluoride	Fluoro

Molecule	Name	Ligand Name
	Cyanide	Cyano
	Hydroxide	Hydroxo
	Nitrite	Nitro

Complex Ligands

<table>
<tr><th>Ligand</th><th>Name</th><th>Classification</th></tr>
<tr><td rowspan="2">
</td><td>Ammine</td><td>UNIdentate</td></tr>
<tr><td>Ethylene diamine</td><td>BIdentate</td></tr>
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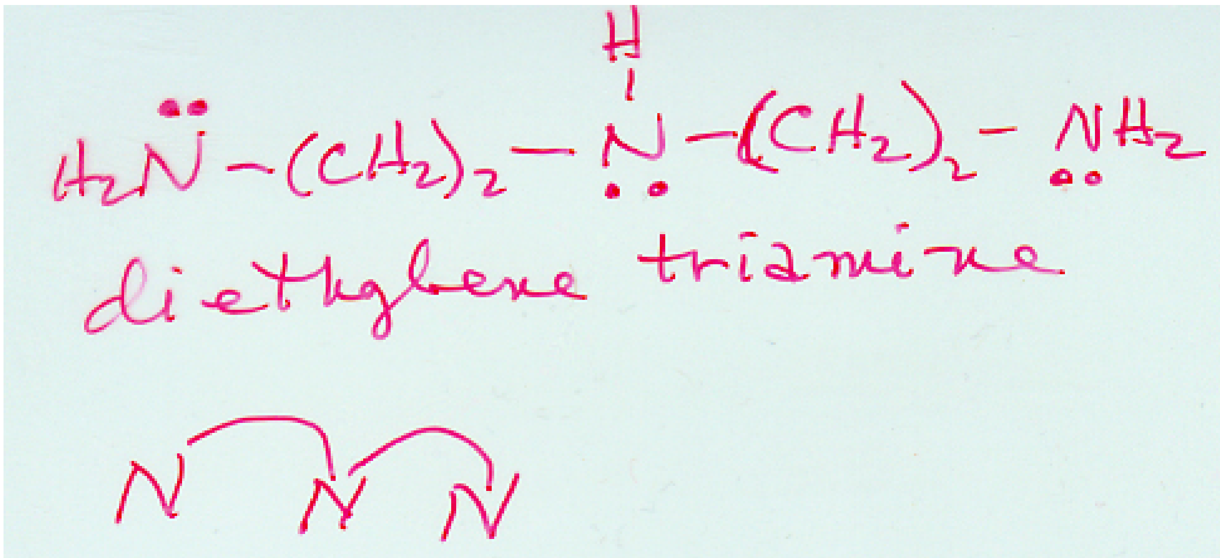
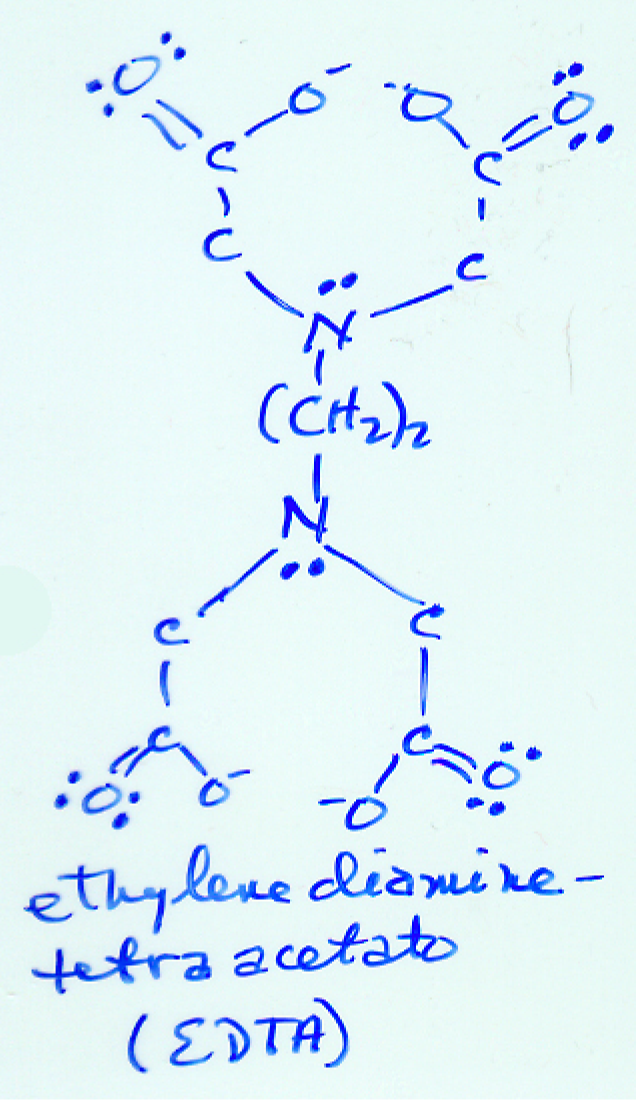
Ligand	Name	Classification
	Diethylene triamine	TRIdentate



Name	Classification
Ethylenediamine-tetra-acetato (EDTA)	SEXIdentate



Naming Metals in Complexes		
Name of Metal	**NOT**	Name in Complex of ANION
Aluminum		Aluminate
Antimony		Antimonate
Chromium		Chromate
Cobalt		Cobaltate
Copper	**Copperate**	CUPRate
Gold	**Goldate**	AURate
Iron	**Ironate**	FERRate
Lead	**Leadate**	PLUMBate
Silver	**Silverate**	ARGENTate
Tin	**Tinnate**	STANNate
Zinc		Zincate

ANION	NAME	Oxidation Number of Metal	Hybridi-zation	Coordination Number
$[Cu(CN)_2]^-$	Dicyanocuprate(I)	+1	sp	2
$[Zn(CN)_4]^{2-}$	Tetracyanozincate(II)	+2	sp^3	4
$[CuCl_5]^{-3}$	Pentachlorocuprate(II)	+2	dsp^3	5
$[Fe(CN)_6]^{-4}$	Hexacyanoferrate(II)	+2	d^2sp^3	6
$[HgCl_3]^-$	Trichloromercurate(II)	+2	sp^2	3

Naming the Metal in CATION Complexes				
CATION	NAME	Oxida-tion Num-ber	Hybrid-ization	Coordin-ation Number
$[Ag(NH_3)_2]^+$	Diamminesilver(I)	+1	sp	2
$(Co(en)_3]^{3+}$	Tris-(ethylenediamine)cobalt(III)	+3	sp^2	3
$[Ni(CO)_4]^0$	Tetracarbonylnickel(0)	0	sp^3	4
$[Cr(OH_2)_6]^{3+}$	Hexaaquachromium(III)	+3	d^2sp^3	6

Effective Atomic Number

$$(At.\ No. - \#\ e^-\ lost\ to\ make\ ion) + \#\ additional\ e^-\ from\ ligand$$

$$E.g.:$$

$$[Fe(CN)_6]^{4-}$$

$$Fe\ At.\ No. - \#\ e^-\ lost + \#\ additional\ e^-\ from\ ligand:$$

$$26 - 2 + 12 = 36$$

$$[Cr(NH_3)_6]^{3+}$$

$$Cr\ \ At.\ No. - \#\ e^-\ \ lost\ + \#\ additional\ \ e^-\ \ from\ ligand$$

$$24 - 3 + 12 = 33$$

$$[Cd(NH_3)_4]^{2+}$$

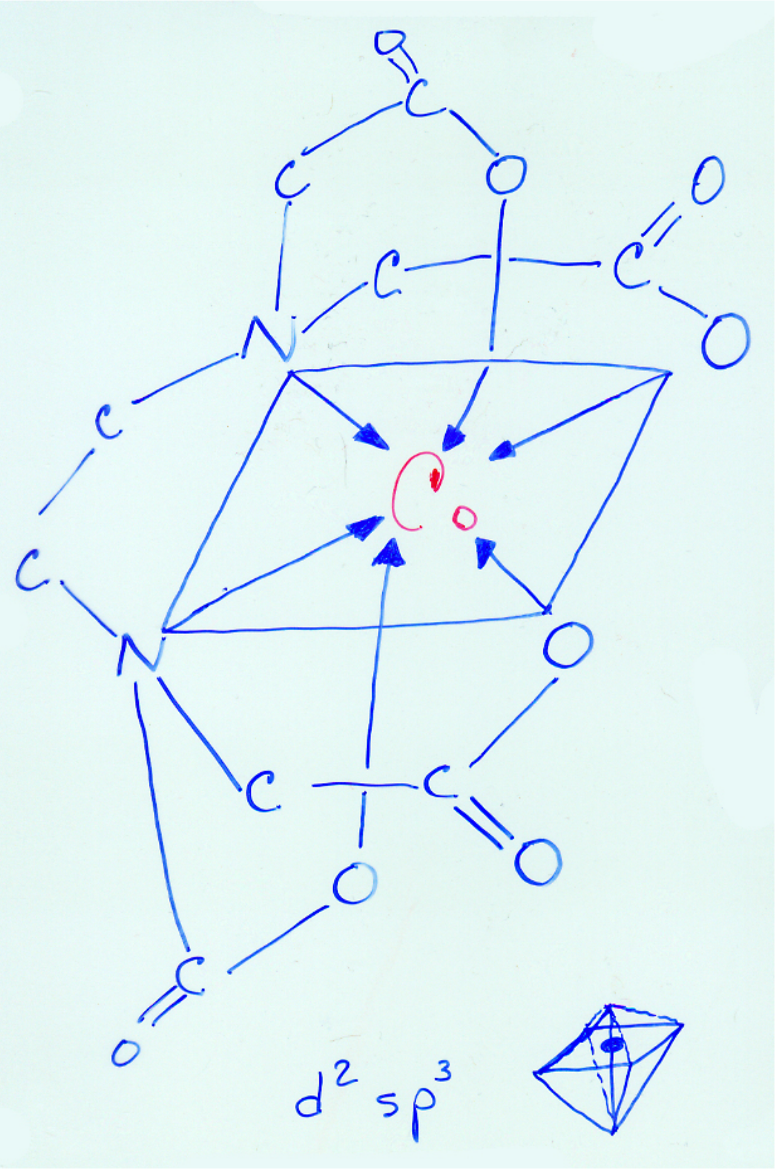
$$48 - 2 + 8 = 54$$

$$[PtCl_6]^{2-}$$

$$78 - 4 + 12 = 86$$

Chelated Compound

d^2sp^3 hybridization
$[Co(edta)]^-$



Nomenclature Rules

1. Name cations before anions
2. In the coordination sphere:
    1. Alphabetize ligands
    2. Use prefixes (not for alphabetic purposes)
3. Anionic ligand suffix = “o”
4. Most neutral ligands have same names except:
    1. NH_3 = ammine
    2. H_2O = aqua
    3. CO = carbonyl
    4. NO = nitrosyl
5. Oxidation number of metals with more than one oxidation number is in “(“ and “)” in Roman numerals as part of the name of the metal.
6. “ate” at the end of a complex = ANION
    1. If neutral = no suffix
    2. If cation = no suffix
    3. Use English stem for name of metal unless is awkward, then use the Latin Root

Examples -- Naming

Complex	Name
$[Ni(CO)_4]$	Tetracarbonyl nickel(0)
$Na_2[Co(OH_2)_2(OH)_4]$	Sodium diaquatetrahydroxocobaltate(II)
$[Pt(NH_3)_4(NO_2)_2](NO_3)_2$	Tetraamminedinitroplatinum(II) nitrate
$[CoCl_6]^{3-}$	Hexachlorocobaltate(III) ion
$[Co(NH_3)_4Cl_2][Cr(C_2O_4)_2]$	Tetraamminedichlorocobalt(II) dioxalatochromate(IV)
$Na[Al(H_2O)_2(OH)_4]$	Sodium diaquadihydroxoaluminate(III)
$Na_2[Pt(CN)_4]$	Sodium tetracyanoplatinate(II)
$[Co(NH_3)_6]_2(SO_4)_3$	Hexaamminecobalt(III) sulfate
$(NH_4)_2[PtCl_4]$	Ammonium tetrachloroplatinate(II)
$[Co(NH_3)_4Cl_2]Cl$	Tetraamminedichlorocobalt(III) chloride
$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquadichlorochromium(III) chloride
$[PtCl_6]^{2-}$	Hexachloroplatinate(IV) ion

Isomers – Two Kinds

- Structural

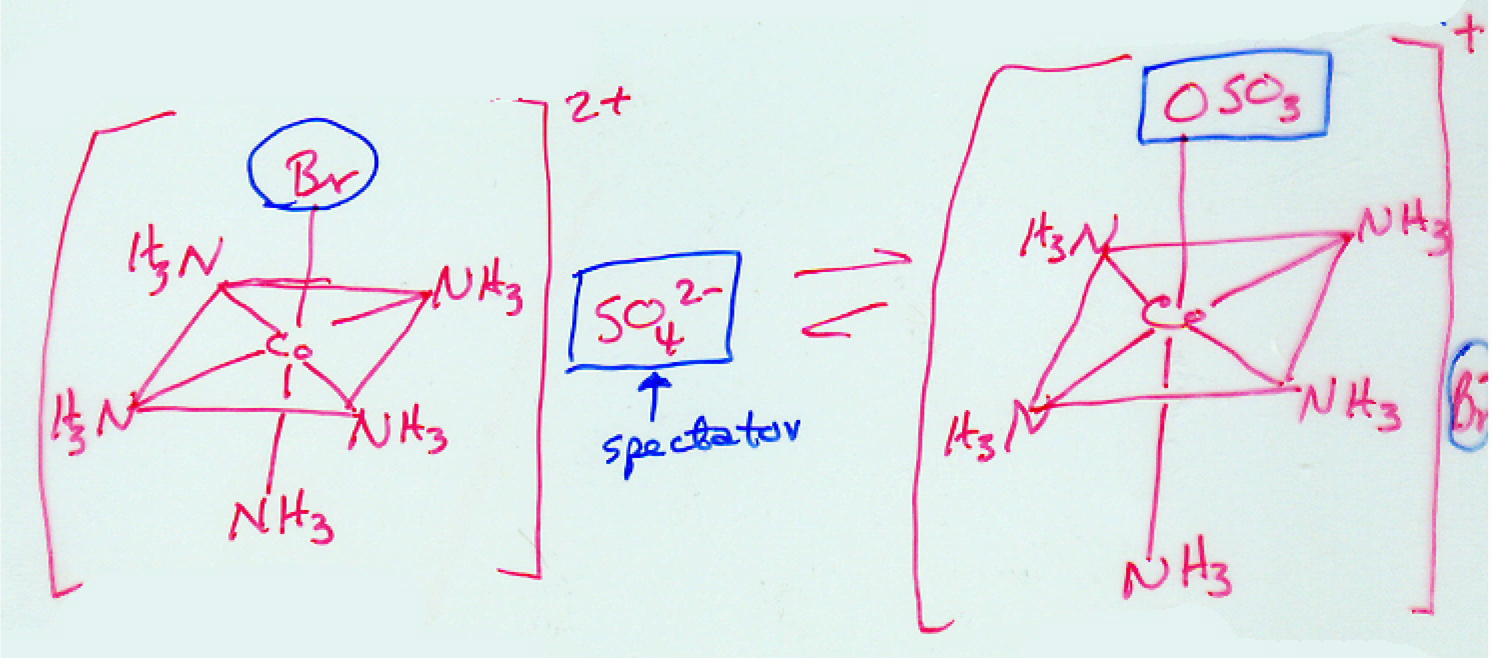
1. Ionization
2. Hydrate
3. Coordination
4. Linkage

- Stereoisomers

1. Geometric (positional)
2. Optical

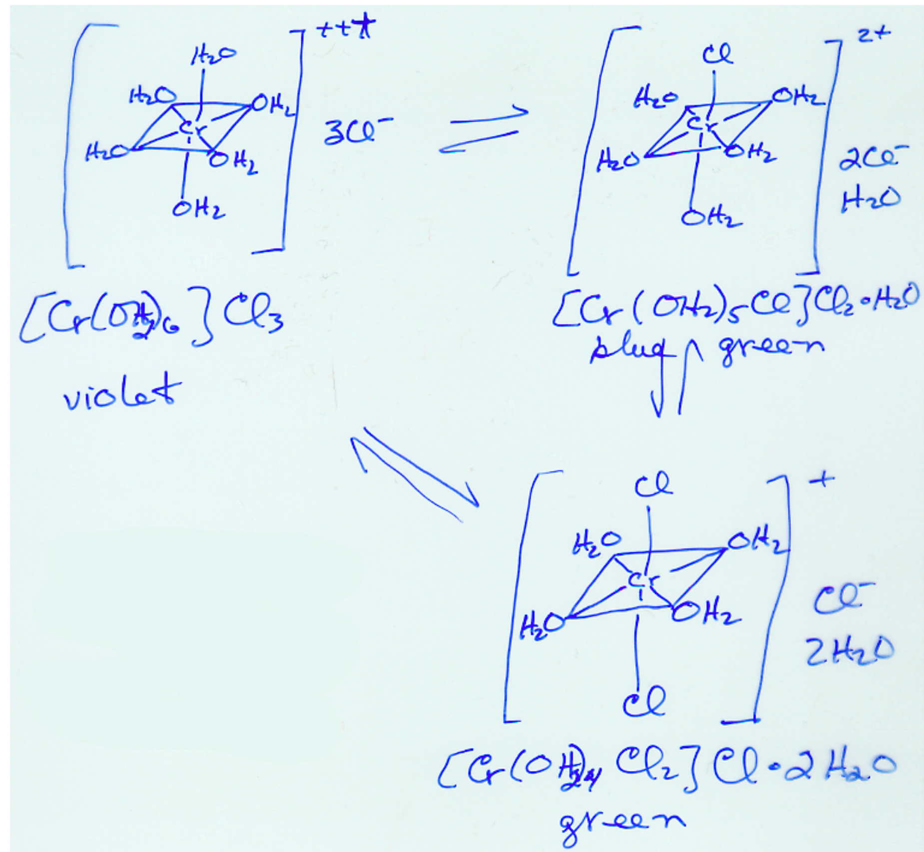
Structural Isomers: Ionization

- Due to the interchange of ions inside and outside the coordination sphere ("[ ]")
- Red violet $[Co(NH_3)_5Br]SO_4$ vs red $[Co(NH_3)_5SO_4]$ Br



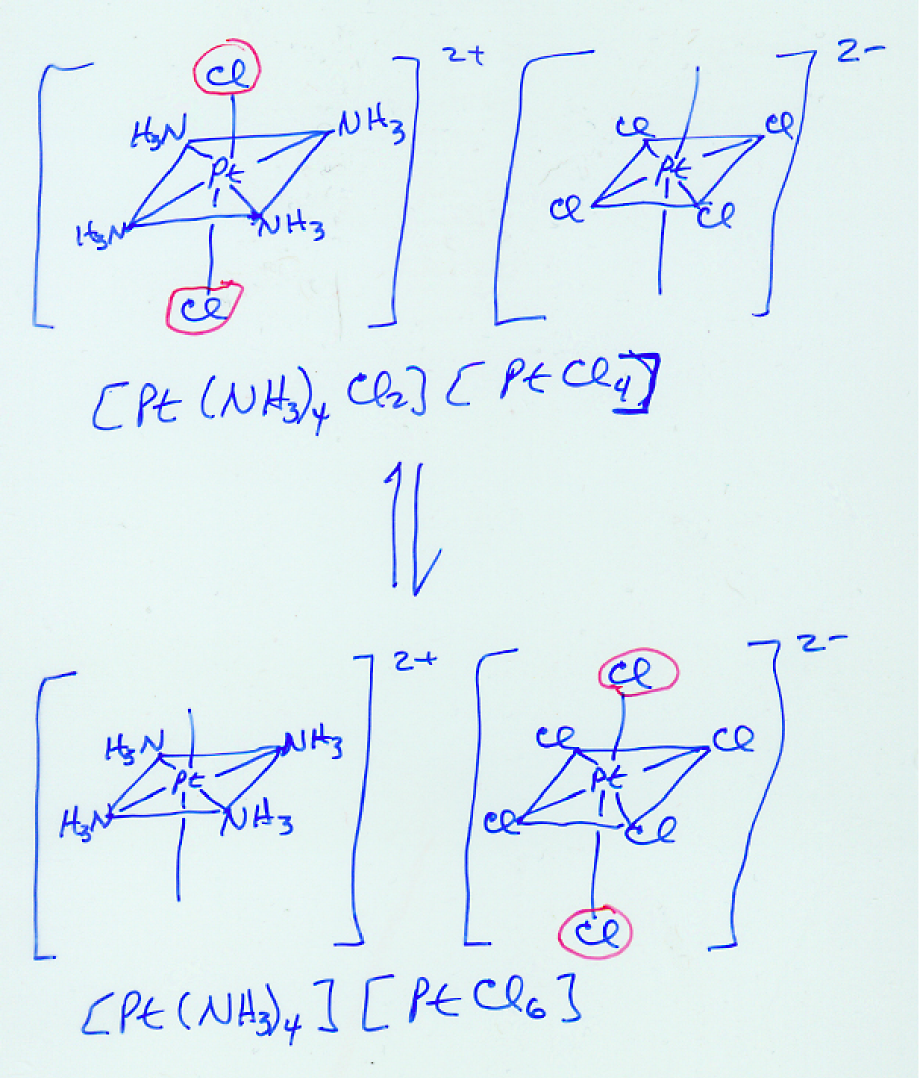
Structural Isomers: Hydrate

- Water inside and outside the coordination sphere
- Violet $[Cr(OH_2)_6]Cl_3$ vs blue green $[Cr(OH_2)_5Cl]Cl_2 \bullet H_2O$ vs green $[Cr(OH_2)_4Cl]Cl_2 \bullet 2H_2O$



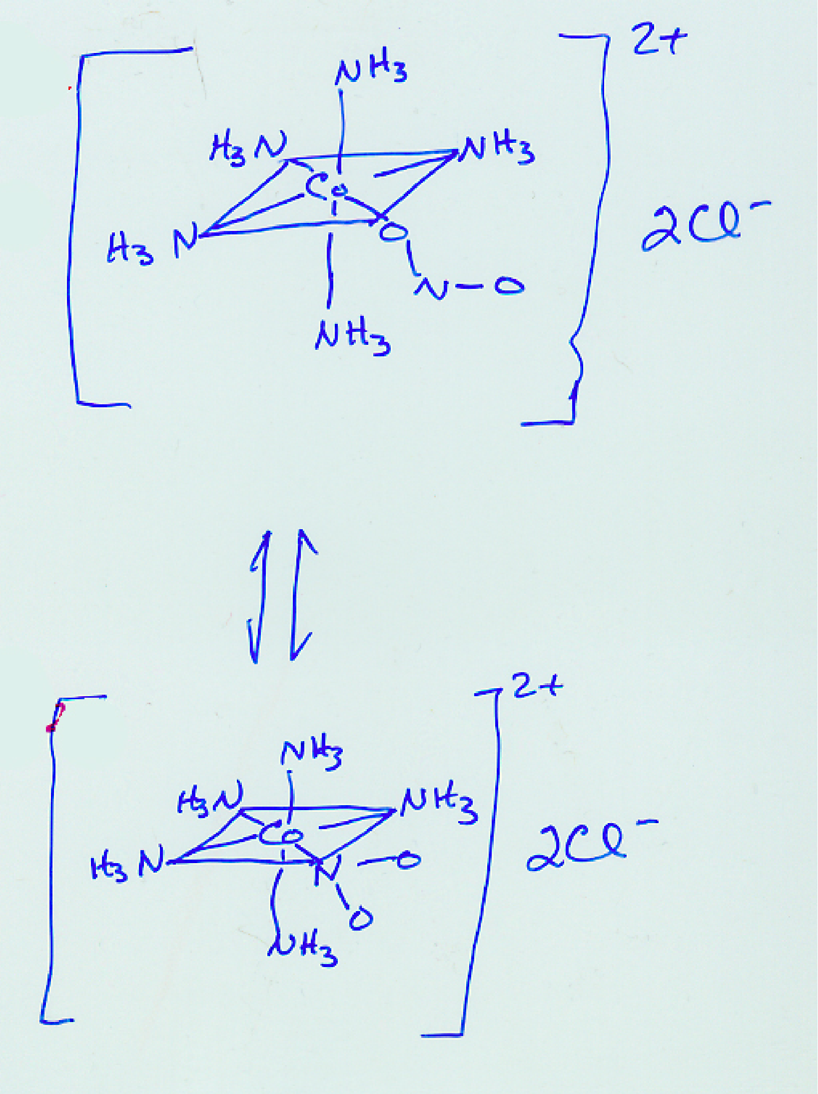
Structural Isomers: Coordination

- An exchange of ligands BETWEEN coordination spheres



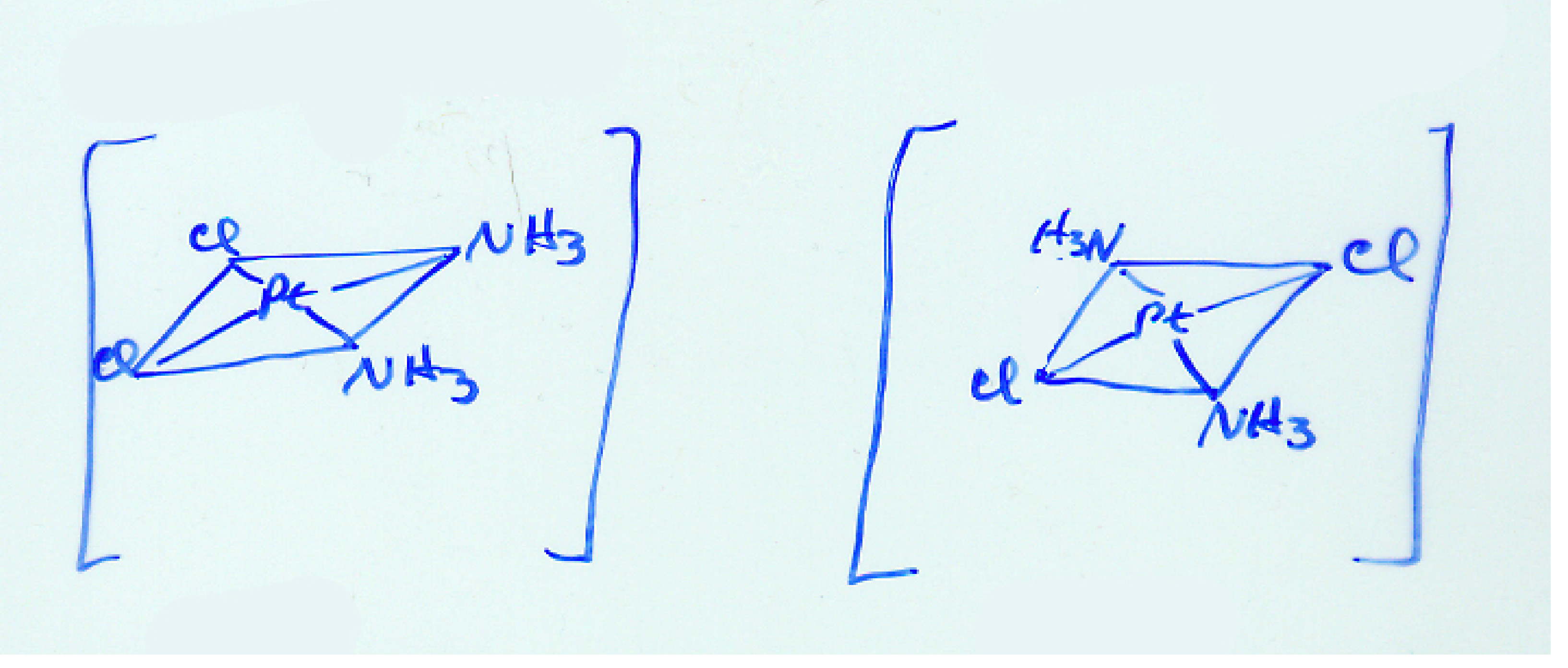
Structural Isomers: Linkage

- Due to some ligands binding in more than 1 manner, e.g.,
- --CN^- (cyano) vs –NC^- (isocyano)
- --NO_2^- (nitro) vs –ONO^- (nitrito)
- Red (top) $[Co(NH_3)_5ONO]Cl_2$ – decomposes in acid vs Yellow (bottom) $[Co(NH_3)_5NO_2]Cl_2$



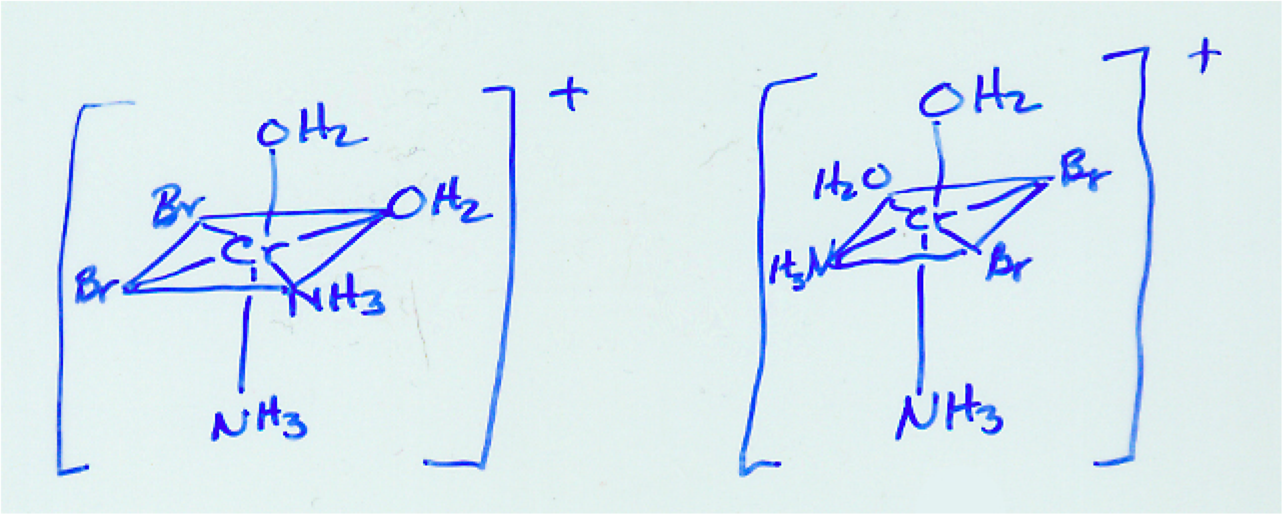
Stereoisomers: Geometric

- Complexes with only SIMPLE ligands can exist as stereoisomers ONLY if their coordination number is 4 or more.
- Positional = geometric
  - cis = adjacent to
  - trans = opposite side of
  - sp^3 hybridization does not form geometric isomerism
- E.g., pale yellow cis-diamminedichloroplatinum(II) (left) vs dark yellow all-trans-diamminedichloroplatinum(II) (right)

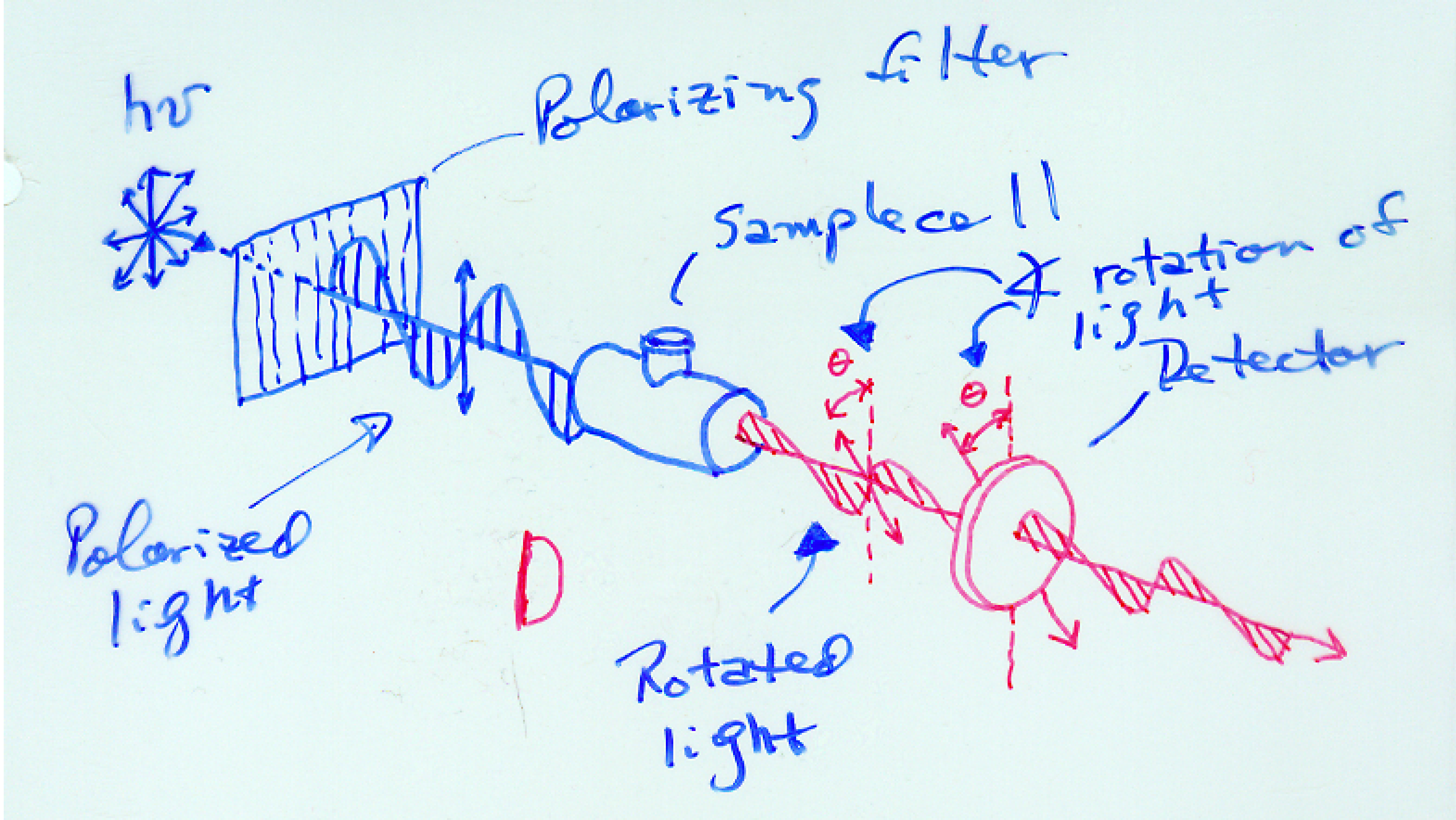


Stereoisomers: Optical

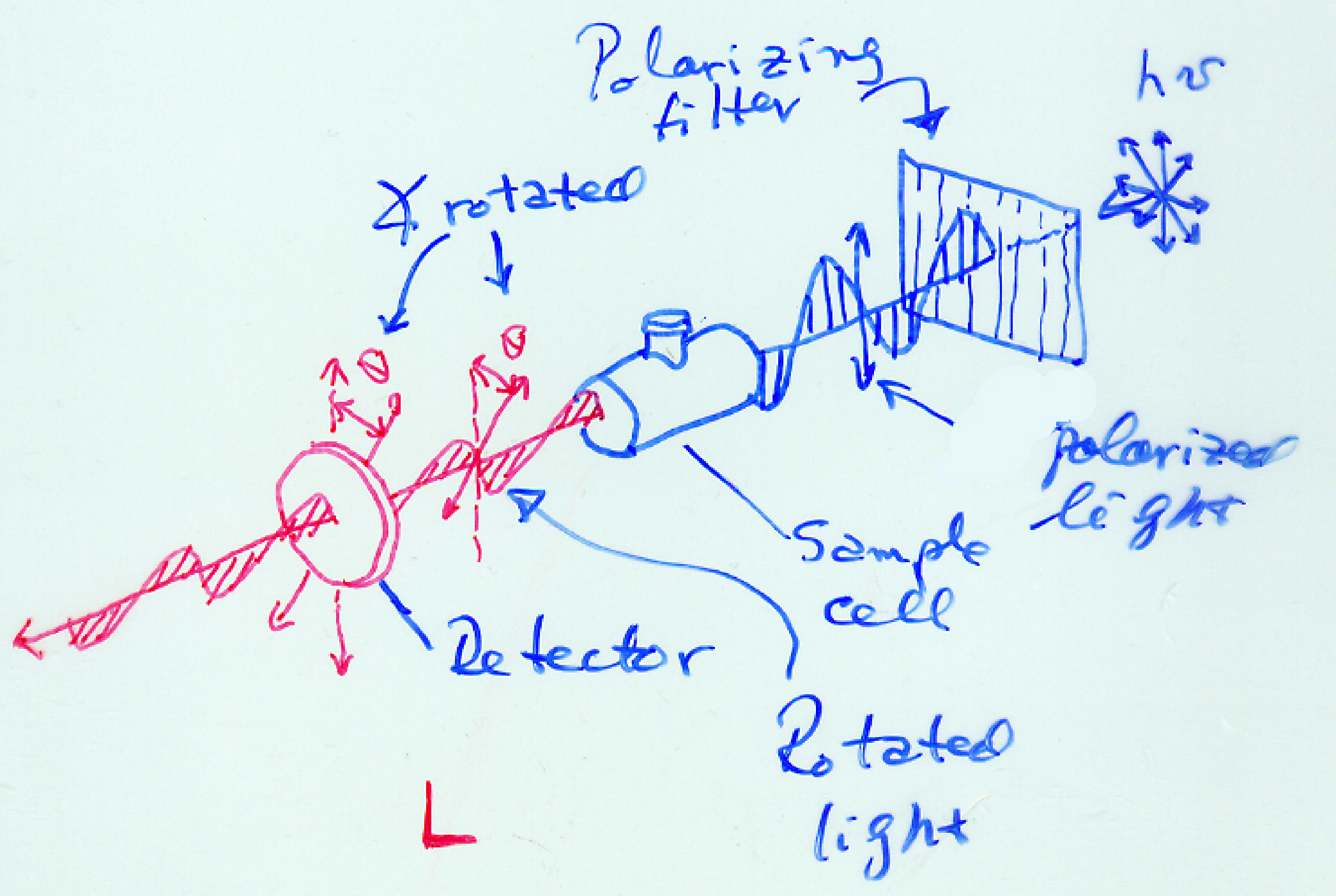
- NON superimposable mirror images of each other; aka enantiomers
- Optical isomers rotate light
  - If to right = dextrorotatory
  - If to left = levorotatory
- E.g., BELOW all cis-$[Cr(NH_3)_2(OH_2)_2Br_2]^+$



Dextrorotatory



Levorotatory



The d-transition Metals

1. All are metals
2. Most are harder than NON transition metals
3. Most are more brittle than NON transition metals
4. Most have higher MP’s than NON transition metals
5. Most have higher BP’s than NON transition metals

Cont'd

5. Their ions/compounds are usually colored
6. Form many complex ions
7. Exhibit MULTIPLE oxidation states
8. Many are paramagnetic (as well as their compounds)
9. Many plus their compounds are catalysts

Uses of Transition Metals

- V – inhibits the Na^+-K^+ pump
- Cr – regulates glucose transport with insulin
- Mn – activates enzymes
- Fe – O_2 transport and electron transfer
- Co – B_{12}
- Ni – cofactor for enzymes
- Cu – redox enzymes and O_2 transport
- Zn – proteinases
- Mo – unknown – but essential
- Cd – unknown, but essential

More uses

- Cis-platin – chemotherapy
- EDTA – heavy metal removal
- As Dyes/pigments:
  - Prussian Blue – $Fe_4[Fe(CN)_6]_3 \bullet xH_2O$
- As catalysts and reagents:
  - Fe and oxides in NH3 synthesis
  - V_2O_5 – SO_3 synthesis
  - $FeBr_3$ – C_6H_5Br synthesis
  - Pt – hydrogenation of unsaturated hydrocarbons

Common Alloys of the d-Transition Metals

Alloy	% compositions
Stainless Steel	Fe – 82.5; Cr – 16.5; C – 0.65; Mn – 0.35
Bronze	Cu – 70-95; Sn – 1-18; Zn – 1-25
Plumber’s solder	Pb – 67; Sn – 33
Sterling silver	Ag – 92.5; Cu – 7.5
US silver coin	Ag – 90; Cu – 10
US gold coin	Au – 90; Cu – 10
18 K yellow gold	Au – 75; Ag – 12.5; Cu – 12.5
14 K yellow gold	Au – 58; Ag – 4-28; Cu – 14-28
18 K white gold	Au – 75; Cu – 3.5; Ni – 16.5; Zn – 5
Dentist Amalgam (1976)	Hg – 50; Ag – 35; Sn – 13; Cu – 1.5; Zn – 0.5

Ground State Configurations: Period 4

4th Period	
Sc	[Ar] $3d^1 4s^2$
Ti	[Ar] $3d^2 4s^2$
V	[Ar] $3d^5 4s^2$
Cr	**→[Ar] $3d^5 4s^1$**
Mn	[Ar] $3d^5 4s^2$
Fe	[Ar] $3d^6 4s^2$
Co	[Ar] $3d^7 4s^2$
Ni	[Ar] $3d^8 4s^2$
Cu	**→ [Ar] $3d^{10} 4s^1$**
Zn	[Ar] $3d^{10} 4s^2$

Ground State Configurations: Period 5

5th Period	
Y	[Kr] $4d^1 5s^2$
Zr	[Kr] $4d^2 5s^2$
Nb	**→ [Kr] $4d^4 5s^1$**
Mo	[Kr] $4d^5 5s^1$
Tc	[Kr] $4d^5 5s^2$
Ru	**→ [Kr] $4d^7 5s^1$**
Rh	[Kr] $4d^8 5s^1$
Pd	**→ [Kr] $4d^{10}$**
Ag	[Kr] $4d^{10} 5s^1$
Cd	[Kr] $4d^{10} 5s^2$

Ground State Configurations: Period 6

6th Period	
La	[Xe] $5d^16s^2$
Hf	[Xe] $4f^{14}5d^36s^2$
Ta	[Xe] $4f^{14}5d^36s^2$
W	[Xe] $4f^{14}5d^46s^2$
Re	[Xe] $4f^{14}5d^56s^2$
Os	[Xe] $4f^{14}5d^66s^2$
Ir	[Xe] $4f^{14}5d^76s^2$
Pt	**→ [Xe] $4f^{14}5d^96s^1$**
Au	[Xe] $4f^{14}5d^{10}6s^1$
Hg	**→ [Xe] $4f^{14}5d^{10}6s^2$**

Comment

- “s” electrons are outside the “d” electrons and are the 1st to be lost in ionization

Magnetisim – In Brief

- Paramagnetic – odd numbers of electrons in outer shell -- metal attracted TO a magnet
- Diamagnetic – even numbers of electrons in outer shell – metal repelled FROM a magnet
- Gouy Balance – discussed in other course material – including the experiment with the magnetic susceptibility balance

Ferromagnetism

- An EXTREME form of paramagnetism
- Causes permanent magnetization
- Exhibited ONLY by Fe, Co, Ni, Gd
- NO HAMMERS!!!!!!!

Ferromagnetism: Requirements

1. Must have an incompletely filled “d” or “f” sub-shell
2. Atoms must not be too close together or ODD electrons will pair up
3. Atoms must not be too far apart or the ODD electrons will not align the electron spins in those atoms.

Non-Zero Oxidation States of 3d Transition Metals	
Sc	+3
Ti	+2, +3, +4
V	+1, +2, +3, +4, +5
Cr	+1, +2, +3, +4, +5, +6
Mn	+1, +2, +3, +4, +5, +6, +7
Fe	+1, +2, +3, +4, +5, +6
Co	+1, +2, +3, +4
Ni	+1, +2, +3, +4
Cu	+1, +2, +3
Zn	+2

Colors of Nitrates

- Of Representative Elements -- colorless
  - Examples: Na, Ca, Mg, Al, Sn (II and IV), Pb
- Of Transition Metals
  - Cr(III): Deep Blue
  - Mn(II): Pale Pink
  - Fe(II): Pale Green
  - Fe(III): Orchid
  - Co(II): Pink
  - Ni(II): Green
  - Cu(II): Blue

Post-Transition Elements

- Zn
- Ga
- Cd
- In
- Sn
- Hg
- Tl
- Pb
- Bi
- Po

Properties of Four

Element	Ga	In	Tl	Pb
Flame Color	Violet	Blue violet	Green	
Outer Electrons	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$	$6s^2 6p^2$
Physical State	SOLID			
Atomic Radius	Smallest →→→→ BARELY →→→→→ LARGEST			
Electronegativity	About the Same			
Comment 1	Greatest liquid state of any element (29.8° C to 2403° C)	Soft, bluish metal, used with Ag and Pb as alloys for heat conductors	Soft heavy metal that resembles Pb	Bluish-white malleable; more dense than Sn
Comment 2	Concentrates in inflamed areas and some melanomas	electronics	TOXIC – NO important practical uses	X-ray protection, battery plates, alloys like solder

Pb – from PbS -- Galena

$$2PbS(s)+3O_2 \xrightarrow[\Delta]{} 2PbO(s) + 2SO_2\uparrow$$

$$SO_2 \text{ reacts with water to form sulfuric acid}$$

$$PbO(s) + C(s) \underset{\Delta}{\overset{\lim estone}{\rightarrow}} Pb(l)+CO\uparrow$$

$$OR$$

$$PbO(s) + CO(g) \underset{\Delta}{\rightarrow} Pb(l)+CO_2\uparrow$$

$$OR$$

$$2PbO(s) + PbS(s) \xrightarrow[\Delta]{} Pb(l) + 2SO_2\uparrow$$

$$\text{and } SO_2\uparrow \text{ used to synthesize sulfuric acid}$$

Pb Uses

- > 50% used in Pb storage batteries
- Pb and Sn are alloyed to make solder (not as much any more – Ag, now) and metal bearings
- Pb + Sb + Sn used to make type metals
- About 30% of all Pb is used to make
- Pigments
  - Red Lead – Pb_3O_4 – traditional primer for Fe and steel
  - White Lead – $2PbCO_3{\bullet}Pb(OH)_2$ – toxic in old houses
- Wood’s Metal – used as valves in automatic sprinklers

Zn – from sphalerite -- ZnS

$$2ZnS\,(s) + 3O_2 \rightarrow 2ZnO\,(s) + 2SO_2\,(g)\ (H_sSO_4\ \ synthesis,\ again)$$

$$\mathrm{Re}\,action\ is\ exothermic\ and\ needs\ no\ heat\ once\ reaction\ is\ going.$$

Reduction of ZnO -- Problem

- $ZnO\ (s) + C\ (s) \rightarrow Zn\ (l) + CO\uparrow$
- NOT spontaneous
- NOT rapid at temperatures less than 906°C (boiling temperature of Zn)
- Reverse actually true < 906°C

Reaction

- $Zn\ (l) + CO_2\ (g) \rightarrow ZnO\ (s) + CO\uparrow$
- The ZnO is due to cooling
- Primary use of Zn: galvanizing Fe and Steel
- Used in alloys
  - Brass: Cu and Zn
  - Bronze: Cu, Sn and Zn
- Used as the container part of dry cell batteries
- Used in pennies (Zn coated with a thin layer of Cu)

Sn – from cassiterite – SnO_2

- Used with Pb for solder (not much any more)
- Used with Cu for bronze
- Primary use: pewter and tin plate
  - Dip sheet Fe or steel in molten Sn OR by electroplating

Three Forms of Sn

- Gray Sn: powdery, non-metallic, structurally similar to diamond
- Malleable Sn: most common – silver white – resistant to air oxidation
  - Malleable tin at temperatures below 13.2°C “converts” to gray tin.
  - This “spreads like an infection” and si called “tin disease” or “tin pest”
- Brittle Sn: not much known about it
- Sn is the BEST metal for organ pipes and the organ pipes of N. Europe were and are subjected to “tin pest”.
- Tin cans: really steel coated with Sn about 0.4-25 μ thick
- Liquid tin used for plate glass: float molten glass on it and allow to solidify

Bi

- Dense metal with yellowish tinge
- Occurs as Bi_2O_3 and Bi_2S_3
- Used in low-melting alloys due to an unusual property: it EXPANDS on freezing
- Low melting Bi alloys are used in fire alarms, electrical fuses, automatic sprinkler systems

Bi

- Bi compounds used in the treatment of stomach and skin diseases
- $(BiO)_2CO_3$: Bismuth subcarbonate
- $(BiO)(C_6H_5O_3)$: Bismuth subsalicylate
- $(BiO)NO_3$: Bismuth subnitrate
- Bi2O3 – alkaline
  - Dissolves in acids to give Bi(III) salts
  - Does NOT dissolve in BASE

$NaBiO_3$

- Sodium bismuthate
- POWERFUL oxidizing agent
- E.g.:

$$Mn^{2+} \text{ (colorless)} + NaBiO_3 \rightarrow MnO_4^- \text{ (purple)}$$

Cd -- Greenockite

- Greenockite is a rare mineral – source of Cd
- Occurs with Zn in ZnS ores
- Separated from Zn by fractional distillation
- Used in cores of nuclear reactors because it's an effective absorber of slow neutrons
- Used in electronics; anti-corrosion (like Zn)
- Also an essential element in human body

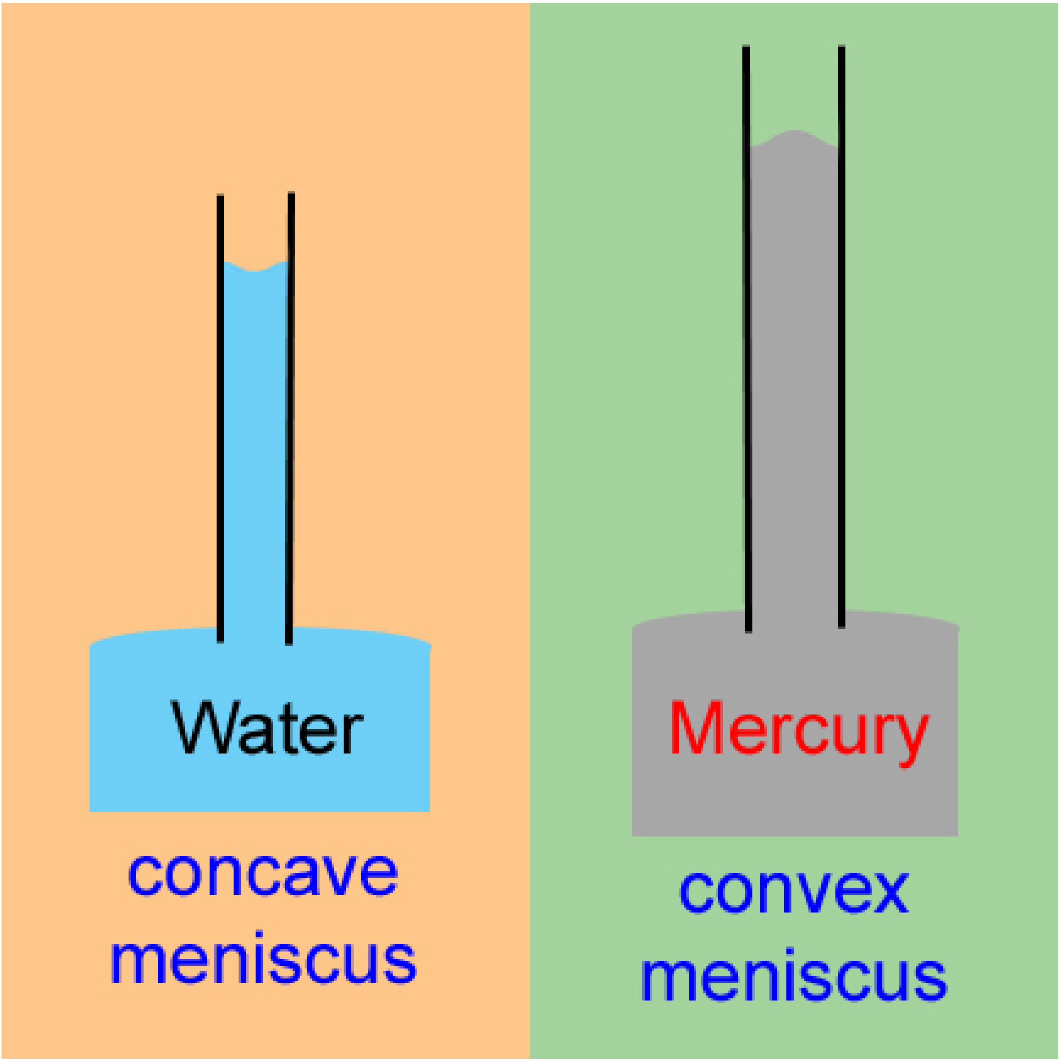
Hg – from cinnabar -- HgS

$$HgS \xrightarrow{roast} Hg(g) \xrightarrow{condense} Hg(l)$$

$$purified\ by\ way\ of\ dilute\ nitric\ acid$$

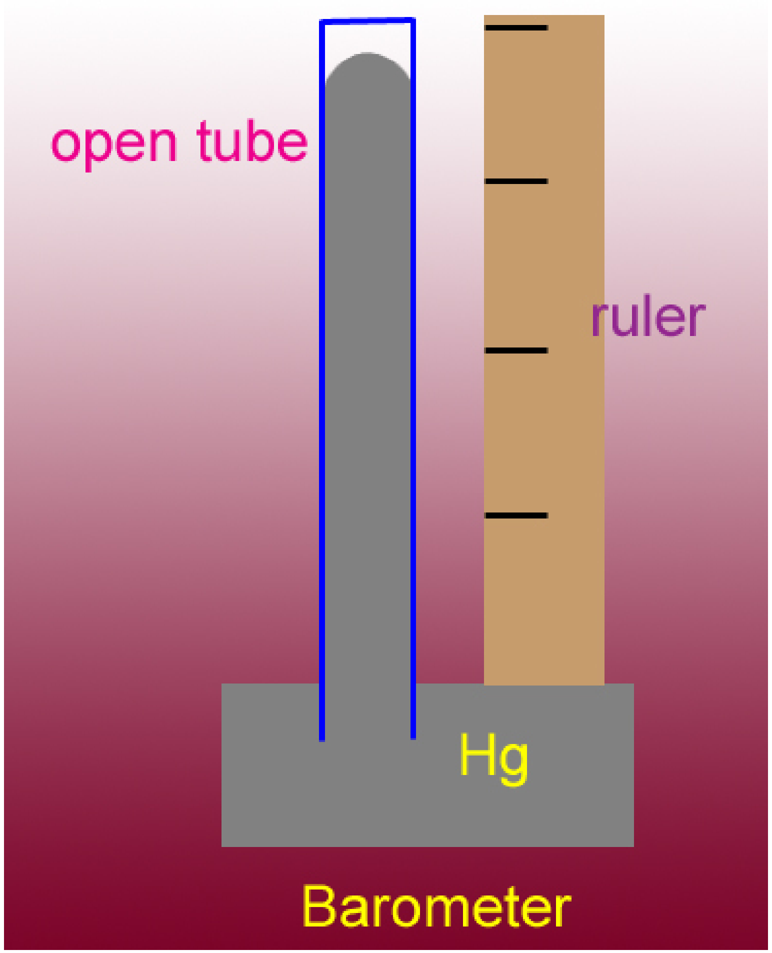
$$Used\ in\ Hg\ barometers$$

Barometer – Meniscus – capillary tubes



Hg Barometer

- $P_{bottom} \alpha Ht_{column} * \rho_{Hg}$
- ρ_{Hg} = 13.6 g/mL
- Hence if water had been used instead of Hg, column would be about 34 feet tall and have a concave meniscus



Amalgams

- Solutions of Hg
- Hg arc lamps plus lanthanide compounds are used for sporting events because they provide “white light” like daylight INSTEAD of unhealthy green light.
- Heavy metal – TOXIC to humans – EVEN THE VAPORS
- 0.2-0.4 g = lethal dose
- React with –SH on proteins
- Treatment: egg whites, milk for gastric ppt’ation

Po

- Intensely radioactive
- Comes from U and Th