Chemistry 1B

Fall 2016

Topics ~~Lectures~~ 17-18

Coordination Chemistry

1

LISTEN UP!!!

- WE WILL ONLY COVER LIMITED PARTS OF CHAPTER 19

(940-944;952-954;963-970)

2

Topics 17-18 Coordination Complexes
Chemistry 1B-AL , Fall 2016

good reasons for studying coordination chemistry

- a 4th type of bonding (coordinate covalent)
- experimental verification of the shape of atomic orbitals (crystal field theory)
- important in biological chemistry
- they are pretty !!!! (glazes) ➡

3

remembering

- Lewis structures
- atomic d-orbitals
- electron configurations
- paramagnetism and diamagnetism

4

what is coordination complex?

a central metal atom or ion to which ligands are bound by coordinate covalent bonds

5

more

- coordinate covalent bond:
  covalent bond where one atom contributes both electrons (in olden times called 'dative' bond)

- ligand:
  ion or molecule which binds to central atom, contributing both electrons to a covalent bond

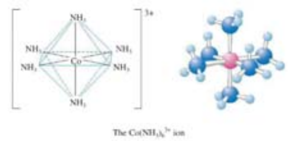
- coordination number:
  how many coordinate covalent bonds around central atom/ion

6

Topics 17-18 Coordination Complexes
Chemistry 1B-AL , Fall 2016

simple example (figure on p. 942)

$[Co(NH_3)_6]\ Cl_3$ (s) salt of complex ion



$[Co(NH_3)_6]Cl_3$ (s) + $H_2O \rightarrow$

$[Co(NH_3)_6]^{3+}$ (aq) + $3Cl^-$(aq)

$[Co(NH_3)_6]^{3+}$ complex ion denoted by [ ]'s

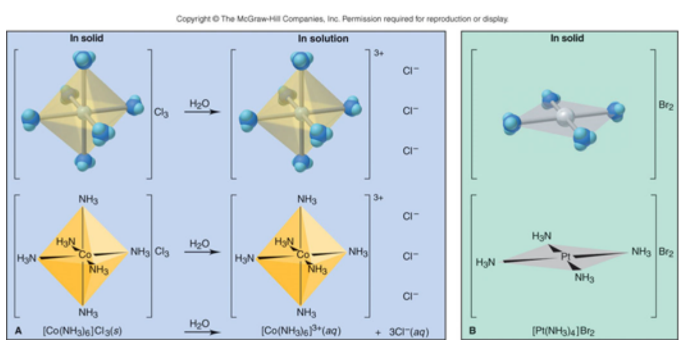
6 NH_3 ligands

metal ion

$3Cl^-$ counter ions

7

figure 23.9 (Silberberg)



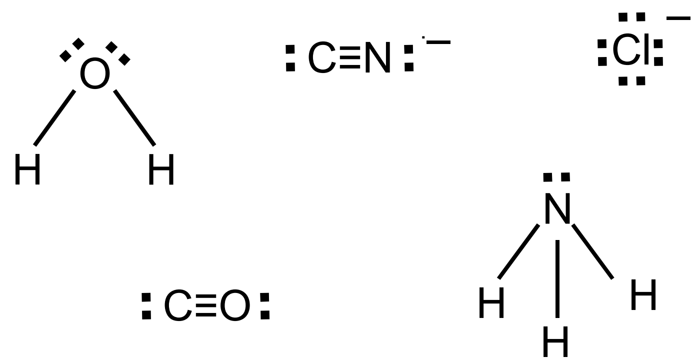
$[Co(NH_3)_6]^{3+}$ ⇨ octahedral

$[Ni(CN)_4]^{2-}$ ⇨ square planar

8

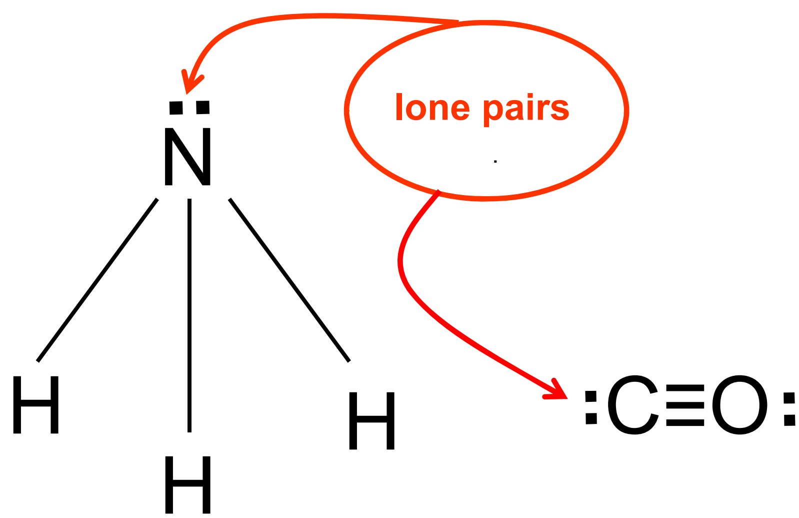
examples of common 'simple' ligands

H_2O, NH_3, Cl^-, CO, CN^-



9

what is common structural feature of ligands



10

Coordinate covalent bond: Lewis acid-Lewis base ***CHEM 1A nr***

Lewis acid

Lewis base

ligand metal

L: M^{+n}

11

Coordinate covalent bond: Lewis acid-Lewis base ***CHEM 1A nr***

Lewis base Lewis acid

ligand metal

L:M^{+n}

12

coordinate covalent bonding

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

Octahedral complex

↓

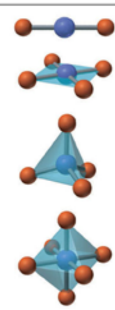
coordination number =6

13

possible geometries of coordination complexes (table 23.6 Silberberg) [see figure 19.6 Zumdahl]

Table 23.6 Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape	Examples
2	Linear	$[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$
4	Square planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$
4	Tetrahedral	$[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$
6	Octahedral	$[Ti(H_2O)_6]^{3+}$, $[V(CN)_6]^{4-}$, $[Cr(NH_3)_4Cl_2]^+$, $[Mn(H_2O)_6]^{2+}$, $[FeCl_6]^{3-}$, $[Co(en)_3]^{3+}$



14

ligands (Table 23.7 Silberberg) [Table 19.13 Zumdahl]

Table 23.7 Some Common Ligands in Coordination Compounds

Ligand Type	Examples							
Monodentate	$H_2\ddot{O}$:	water	$:\ddot{F}:^-$	fluoride ion	$[:C{\equiv}N:]^-$	cyanide ion	$[:\ddot{O}{-}H]^-$	hydroxide ion
	$:NH_3$	ammonia	$:\ddot{Cl}:^-$	chloride ion	$[:\ddot{S}{=}C{=}\ddot{N}:]^-$ (or)	thiocyanate ion	$[:\ddot{O}{-}\ddot{N}{=}\ddot{O}:]^-$ (or)	nitrite ion

monodentate

atom forming coordinate covalent bond indicated in **BLUE**

15

ligands (Table 23.7 Silberberg) [see Table 19.13 Zumdahl]

Bidentate

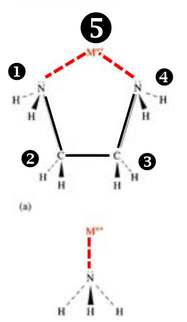
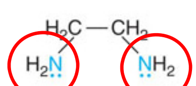
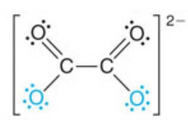


Figure 20.7
(a) The bidentate ligand ethylenediamine can bond to the metal ion through the lone pair on each nitrogen atom, thus forming two coordinate covalent bonds.
(b) Ammonia is a monodentate ligand.



ethylenediamine (en)

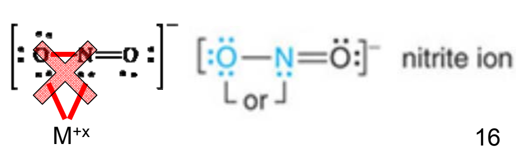


oxalate ion

bidentate

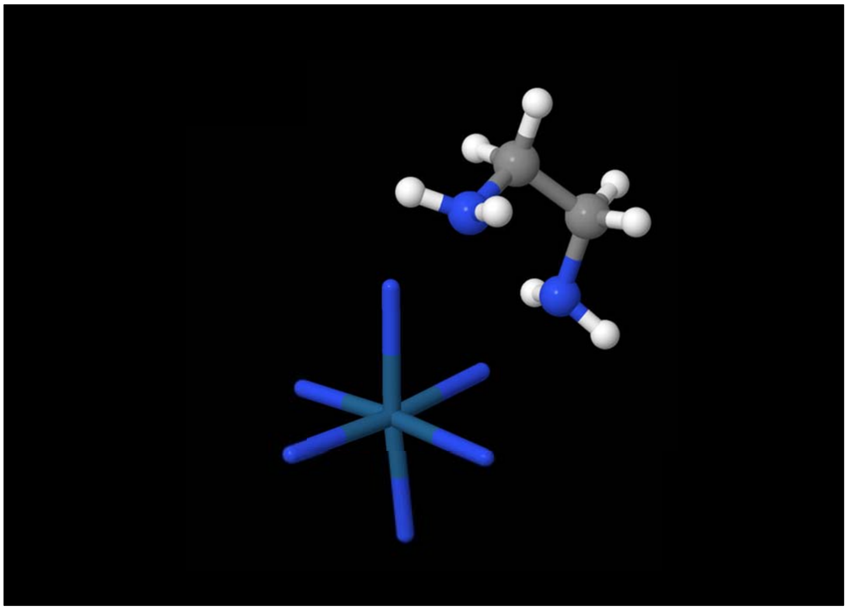
atoms forming coordinate covalent bonds indicated in **BLUE**

multi-dentate 5 or six membered ring with M^+



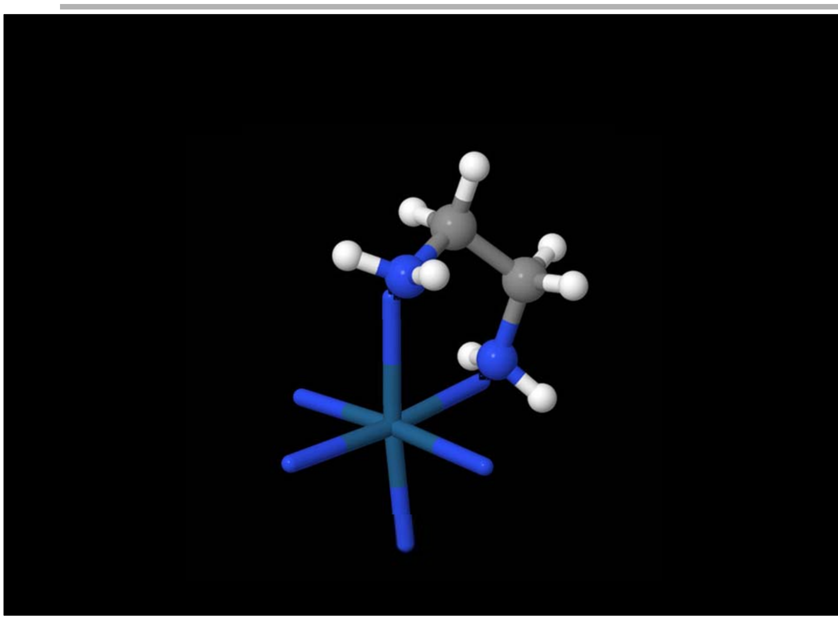
16

*ethylene diamine **bidentate** ligand*



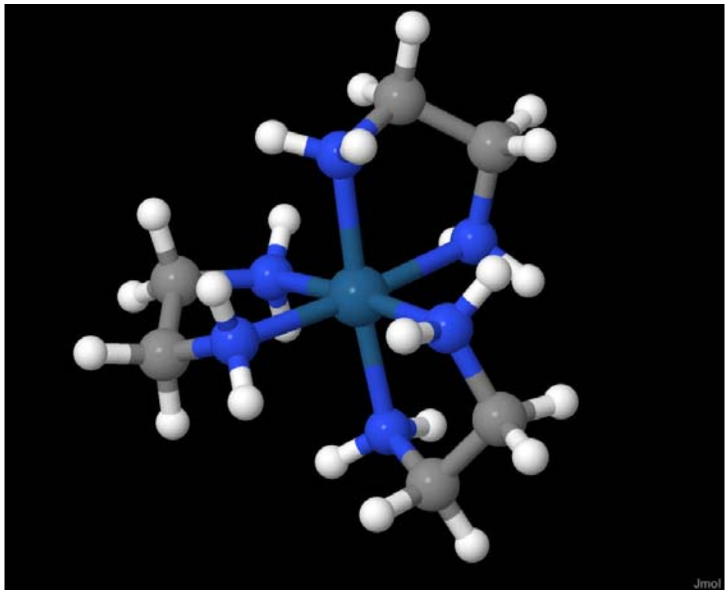
17

*ethylene diamine **bidentate** ligand*



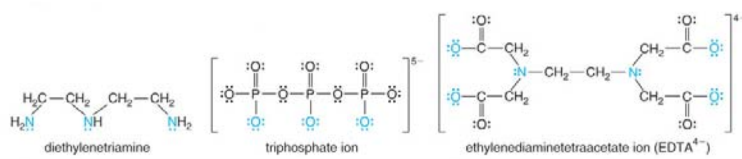
18

$[Cr(en)_3]^{3+}$ octahedral complex

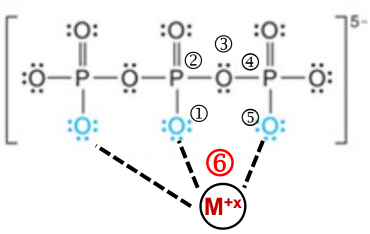


19

ligands (Table 23.7 Silberberg) [see Table 19.13 Zumdahl]



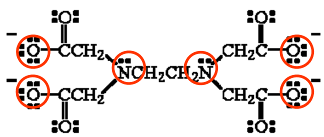
polydentate



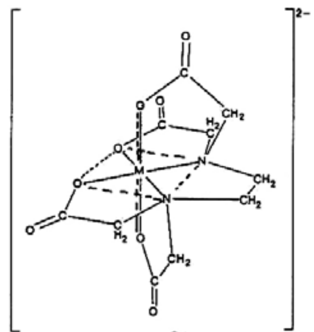
atoms forming coordinate covalent bonds indicated in **BLUE**

20

EDTA a chelate (claw!!)



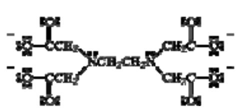
hexadentate

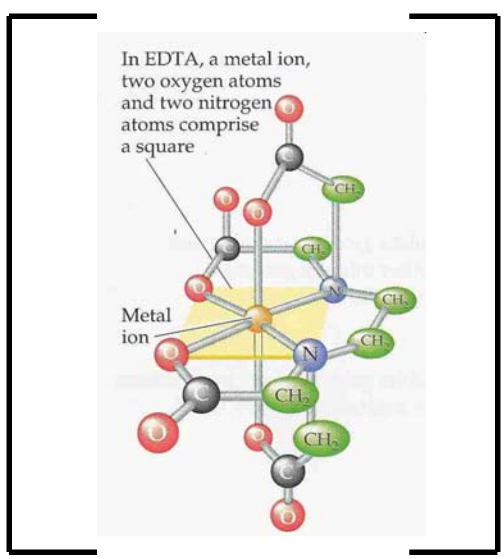


M=Pb^{2+}

21

more $EDTA^{4-}$



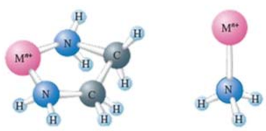


2-
for Fe^{2+}

22

Topics 17-18 Coordination Complexes
Chemistry 1B-AL , Fall 2016

Table 19.13 , Figure 19.7



(a) (b)

FIGURE 19.7

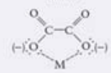
(a) The bidentate ligand ethylenediamine can bond to the metal ion through the lone pair on each nitrogen atom, thus forming two coordinate covalent bonds. (b) Ammonia is a monodentate ligand.

TABLE 19.13

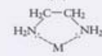
Some Common Ligands

Type	Examples	
Unidentate/monodentate	H_2O NH_3 CN^- NO_2^- (nitrite)	SCN^- (thiocyanate) OH^- X^- (halides)
Bidentate	Oxalate	Ethylenediamine (en)
Polydentate	Diethylenetriamine (dien) $H_2N-(CH_2)_2-NH-(CH_2)_2-NH_2$ Three coordinating atoms	
	Ethylenediaminetetraacetate (EDTA) Six coordinating atoms	

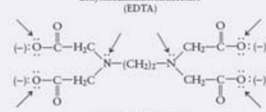
Oxalate:



Ethylenediamine (en):



Ethylenediaminetetraacetate (EDTA):



23

---

determining: num ligands charge oxidation state d-electrons

given [Co(NH_3)$_n$] Cl_3 is salt of octahedral complex

- **coordination number=6 since octahedral**
- **n=6** since NH_3 is monodentate ligand
- **3^+** charge on complex from counterion: 3 Cl^-
- **Co^{3+}** oxidation state of metal from charge on complex and zero charge on NH_3 ligands
- **d^6** d-electrons from aufbau principle FOR CATIONS

24

other examples

$K_3[Fe(CN)_{\mathbf{n}}]$ octahedral

$[Co(en)_{\mathbf{n}}]Cl_3$ octahedral

$Na_2[Ni(CN)_{\mathbf{n}}]$ square planar

25

~~*Sections 19.1-19.2, 19.4 (pp 940-951;956- 963)*~~ ***(don't fret)***

- General factoids about transition metals
- Nomenclature
- Isomerism

FIGURE 19.4
A bicycle with a titanium frame.

Manganese nodules on the sea floor.

FIGURE 19.15

26

~~Section 19.5 Localized Electron model (pp 963-964)~~ *(don't fret)*

hybridization involving d-orbitals:

d^2sp^3 six octahedrally oriented hybrids
dsp^3 four square planar hybrids

27

Crystal Field Theory of Coordination Complexes

magnetic properties
and
pretty colors

(Pp 964-970)

28

Topics 17-18 Coordination Complexes
Chemistry 1B-AL , Fall 2016

have covered worksheet 10 I-III

Learning Objectives and Worksheet X

Chemistry 1B-AL Fall 2016

Lectures (17-18) Coordination Chemistry

WE WILL ONLY COVER LIMITED PARTS OF CHAPTER 19. (940-944; 952-954,963-970).

Supplementary video: Introduction to Ligands and Complexes http://youtu.be/EufPZFAwWco

Great introduction to coordination complex chemistry: http://www.chem.purdue.edu/gchelp/cchem/whatis2.html

The next two class sessions will be devoted to an introduction to a fourth type of bonding, the coordinate covalent bond. Transition metal coordination complexes are an important class of molecules that exhibit this type of bonding and are important in a number of areas including material science and biology. In addition we will study "crystal field theory" that describes the electron configuration of d-electrons in transition metal complexes and, in making predictions about the chromatic and magnetic properties of transition metal complexes, will provide for us experimental correlation of the 'reality' of d-orbital shapes which we discussed in chapter 12.

I. Introduction

1. A coordination complex is composed of a central atom or ion (often a transition metal) and molecules (or ions) called __ligands__ that are bound to the central atom by __coordinate covalent__ bonds where both __electrons__ are contributed by the __ligand__.
2. In the coordination complex $[Cu(CN)_4]^{3-}$ the central atom/ion is __Cu^+__, the ligands are __$(CN)^-$__, and the coordination number is __4__.

Homework: 55, 516

II. Common Ligands

1. In order to form a coordinate covalent bond the ligand must generally have one or more __non-bonding pairs of electrons__.
2. Why is ethylene diamine $H_2NCH_2CH_2NH_2$ with two pairs of non-bonding electrons a bidentate ligand while cyanide $(CN)^-$ with two pairs of non-bonding electrons can only form one coordinate covalent bond?

   In ethylene diamine the two lone-pair atoms are separated by two other atoms and thus could form a five-membered ring in bonding at two different coordination sites on the central atom. The five-membered ring is sterically stable with regard to 'ring strain'.
   In the cyanide ion the two lone-pairs are on adjacent atoms and thus, if they were both to form coordinate covalent bonds, they would be required to form a sterically unstable three-membered ring.

III. Formulas, oxidation states, d-electrons in coordination compounds

1. To calculate the number of ligands in a coordination complex you must
   i. know the coordination number of the complex from the __geometry__ of the complex ion, (or perhaps vice versa)
   ii. and the __number of coordinate covalent bonds, the 'dentateness'__ of each ligand.
2. To calculate the total charge on the complex ion you must know the total charges of the __counterions__ forming the neutral ionic 'salt' along with the complex ion.
3. To calculate the oxidation state of the metal ion you must
   i. know the __total charge__ of the complex ion
   ii. and the __charge on each ligand__ (multiplied by the number of ligands)
4. To calculate the number of d-electrons on the metal ions one applies the oxidation state of the metal and the Aufbau principle for positive ions.
5. A tetrahedral complex of $[CuCl_x]^{2-}$ has a total charge of 2−
   i. The number of chloride ligands, x, is __4__.
   ii. The oxidation state of the $Cu^?$ ion is __2+__.
   iii. The number of d-electrons on the $Cu^?$ ion is __9__.

Further links to the orientation of d-orbitals relative to coordination sites:

Octahedral: http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/Jmol/CrystalField/CFT_OrbsOctahedral

Several geometries: http://www.chem.uwimona.edu.jm:1104/courses/CFT_Orbs.html

Hemoglobin: http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/WWW_other_links/ox_deox_hemo.htm

IV. Magnetic and chromatic properties of transition metal complexes

see: https://www.youtube.com/watch?v=xNXRSE7pxXM

this video (clickers Q's next class) cover: ***worksheet 10 IV***

IV. Magnetic and chromatic properties of transition metal complexes

see: https://www.youtube.com/watch?v=xNXRSE7pxXM *recommended !!!!*

IV. Magnetic and chromatic properties of transition metal complexes

see: https://www.youtube.com/watch?v=xNXRSE7pxXM

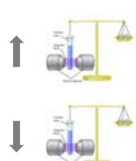
31

basic aims of this video presentation

crystal-field theory of transition metal coordination complexes

"reality" of the shapes of d-orbitals

- why are 'free' transition metal ions colorless ?
  but
  transition metal ions in coordination complexes are often colored ?

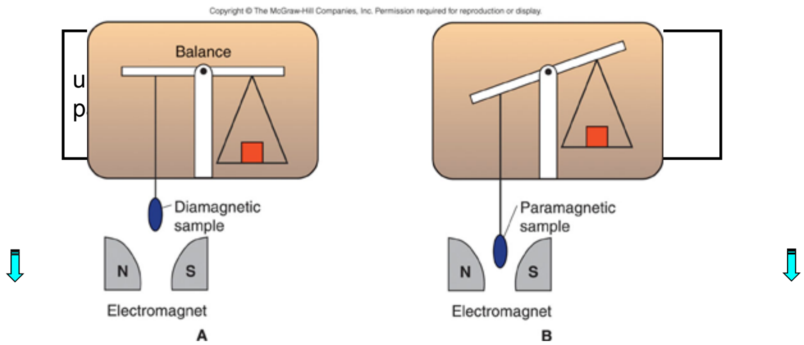


- why are some transition metal complexes diamagnetic?
- and others are paramagnetic?

32

paramagnetism vs diamagnetism (Gouy balance)

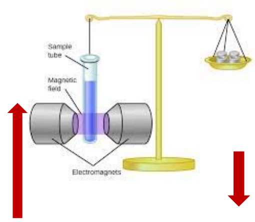
diamagnetic paramagnetic



strength of paramagnetism depends on number of unpaired electrons

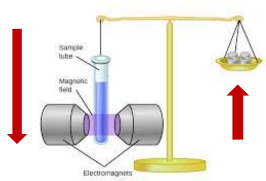
33

crystal field theory and magnetic properties $[Co(NH_3)_6]^{3+}$ vs $[Co(F)_6]^{3-}$



$[Co(NH_3)_6]^{3+}$ is diamagnetic

but



$[Co(F)_6]^{3-}$ is paramagnetic

34

crystal field theory and color

- most electronic excitations in UV
  (H 1s → H 2p λ=121 nm)

- Co^{3+} [Ar]$3d^6$ → Co^{3+} [Ar]$3d^5 4s^1$ (λ=75.3 nm) **UV**
  NH_3 → NH_3^* (excited state) (λ=216 nm) **UV**

Co^{3+} and NH_3 are colorless !!!

but in coordination complex

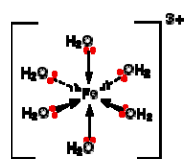
- $[Co(NH_3)_6]^{3+}$ → excited state* (λ=430 nm, absorbs 'indigo')

$[NH_3)_6]^{3+}$ appears yellow-orange !!

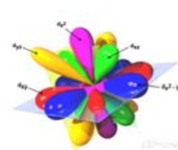
35

crystal field theory

1. the ligands form coordinate covalent electron pair σ-bonds with the metal ion/atom, the ligand contributing both electrons



2. crystal field theory addresses the effects of the presence of these ligands on the d-electrons of the metal ion by considering the electrostatic (repulsive) interaction of the ligand non-bonding pairs with the d-electrons.



36

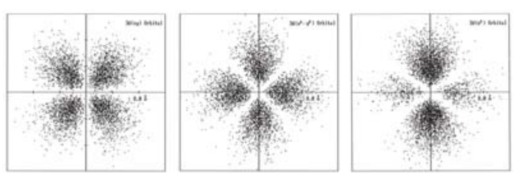
limiting the playing field

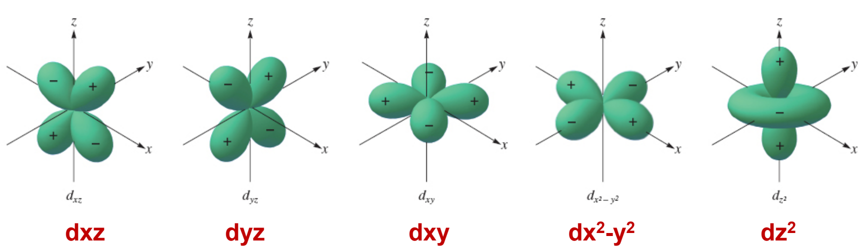
- Crystal field theory- an electrostatic approach to ligand-metal d-orbital interactions
  (more complicated ligand-field and m.o. approaches lead to similar predictions)

- Only responsible for octahedral complexes
  (other geometries follow similar considerations)

37

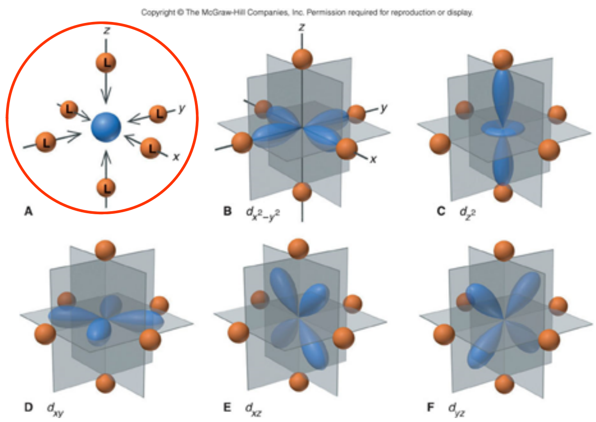
remember atomic d-orbitals (figure 12.21)





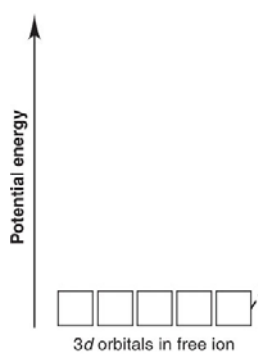
38

*metal ion d-obitals in **octahedral** complex*
(Silberberg fig. 23.17; Zumdahl fig. 19.21)



39

what happens to energies of d-orbitals when ligands bind to metal ion? (fig 23.18)

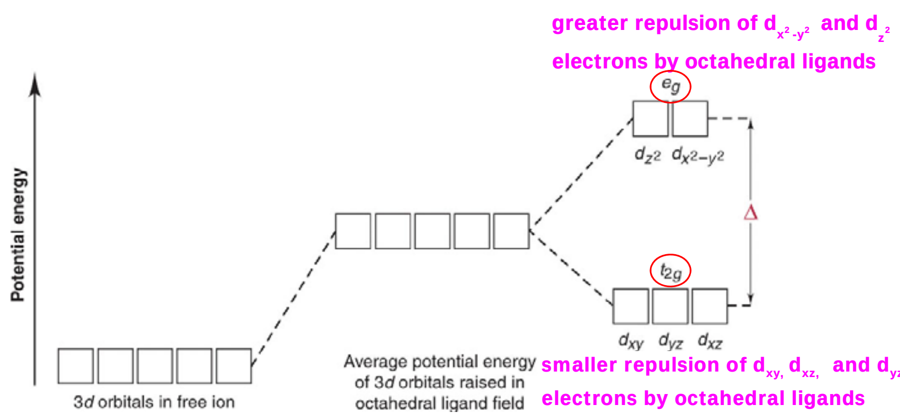


average ligand repulsion
for metal d-electrons

would each d-electron
be repelled the same?

40

what happens to energies of d-orbitals when ligands bind to metal ion? (fig 23.18)



average ligand repulsion for metal d-electrons

would each d-electron be repelled the same?

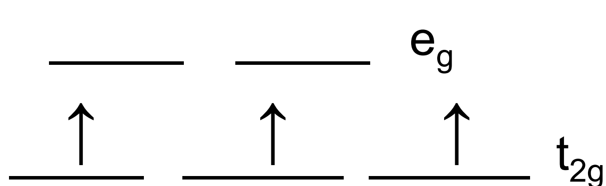
41

filling of d-orbitals in octahedral complex: $d^1 \rightarrow d^3$ ground state

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

V^{2+}

d^3



configuration: $(t_{2g})^3$ ↿ ↿ ↿

paramagnetic: three unpaired electrons

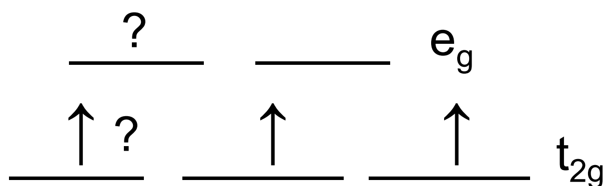
42

filling of d-orbitals in octahedral complex: $d^4 \rightarrow d^{10}$ ground state

$[Cr(H_2O)_6]^{2+}$ vs $[Cr(CN)_6]^{4-}$

Cr^{2+} Cr^{2+}

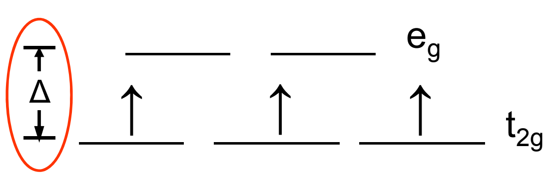
d^4 d^4



where does electron 4th go ?

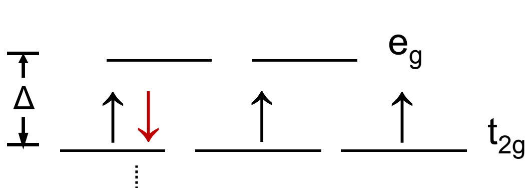
43

Δ vs ($E_{pairing}$) : two possibilities for d^4



$t_{2g}^3 e_g$

costs Δ *(in energy)*
but e's
remain unpaired



t_{2g}^4 ↿⇂ ↿ ↿

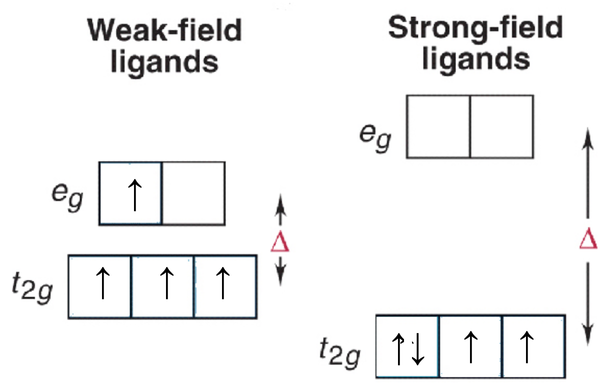
costs $E_{pairing}$
but
not Δ

$E_{pairing}$= higher energy for paired vs unpaired electrons

44

strong and weak field ligands: lowest orbitals vs unpaired spins
Δ vs ($E_{pairing}$) (Silberberg fig 23.18)

d^4 d^4



$[Cr(H_2O)_6]^{2+}$

($E_{pairing}$) > Δ
small Δ favors filling
maximum unpaired spins

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

Δ > ($E_{pairing}$)
large Δ favors filling
lowest orbitals first

45

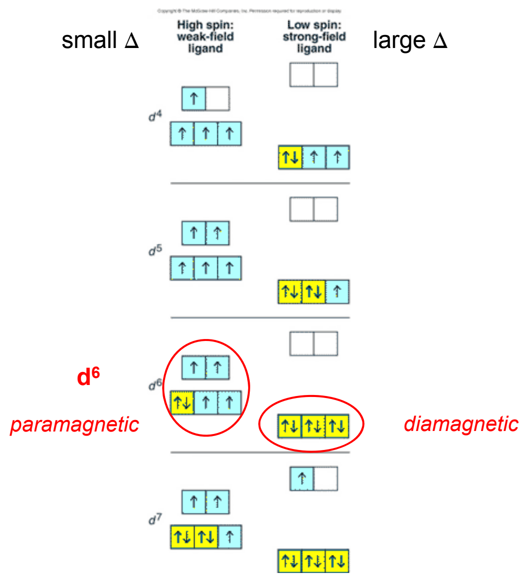
$[Cr(H_2O)_6]^{2+}$ vs $[Cr(CN)_6]^{4-}$

- $[Cr(H_2O)_6]^{2+}$, d^4, weak-field ≡ high spin,
  ↑ –
  ↑ ↑ ↑ $t_{2g}^3 e_g^1$
  4 unpaired electrons, paramagnetic

- $[Cr(CN)_6]^{4-}$, d^4, strong-field ≡ low spin,
  – –
  ↑↓ ↑ ↑ t_{2g}^4
  2 unpaired electrons, paramagnetic

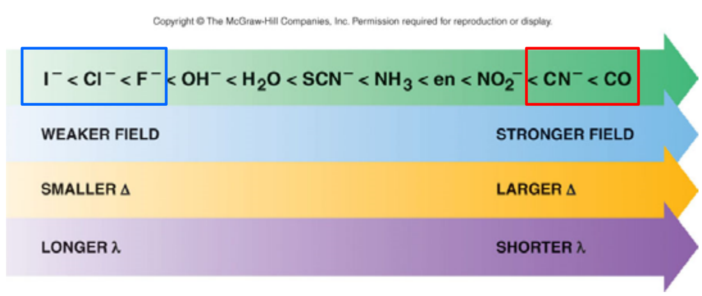
46

high-spin vs low-spin complexes: $d^4 \rightarrow d^7$ (Silberberg fig. 23.24)



47

spectrochemical series (fig. 23.22 Silberberg; Zumdahl p. 961)



know: CN^-, CO strong (high) field
F^-, Cl^-, I^- (halogen anions) weak (low) field
if using others you would be told which

48

crystal field theory (pp 959-955)

- How are the magnetic properties of transition metal complexes related to the shape of d-orbitals?

- Why are transition metal complexes colored?

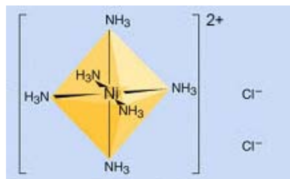
49

color

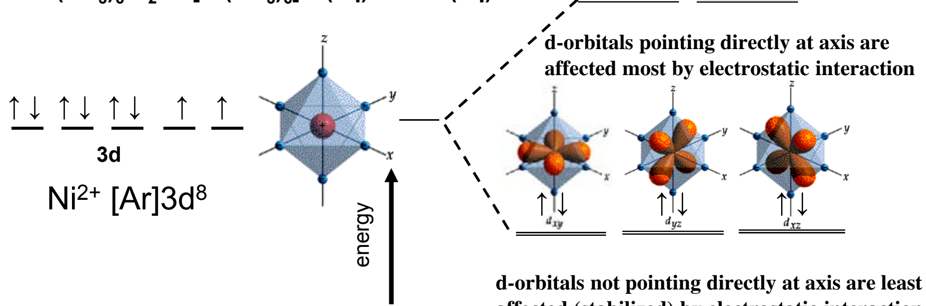
Color in octahedral complex ions arises from $t_{2g} \rightarrow e_g$ electronic transitions (excitations) that have energies corresponding to photons in the visible wavelengths.

50

d-Orbitals and ligand Interaction (octahedral field)



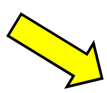
$Ni(NH_3)_6Cl_2 \xrightarrow{H_2O} [Ni(NH_3)_6]^{2+}\,(aq) + 2Cl^-\,(aq)$

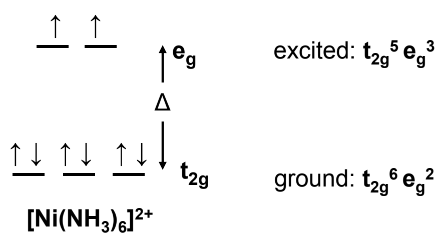


ibchem.com/IB/ibfiles/periodicity/per_ppt/**Crystal_field_theory**.ppt

51

absorption of visible light in octahedral transition metal complexes





- larger Δ's correspond to absorbing shorter wavelengths
- how does the wavelength absorbed relate to the color perceived for various transition metal complex ions ?
  [next class !!]

52

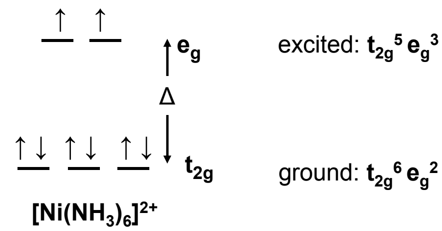
53

Perception of the Color of Objects

an addendum to Crystal Field Theory

54

absorption of visible light in octahedral transition metal complexes



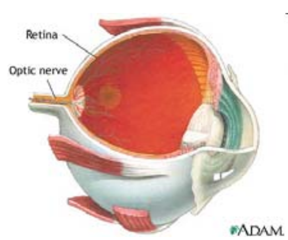
- larger Δ's correspond to absorbing shorter wavelengths
- how does the wavelength absorbed relate to the color perceived for various transition metal complex ions ?

55

why are some molecules colored ? (spectroscopy lectures later)

human vision and chemistry LATER in spectroscopy → ***not now***

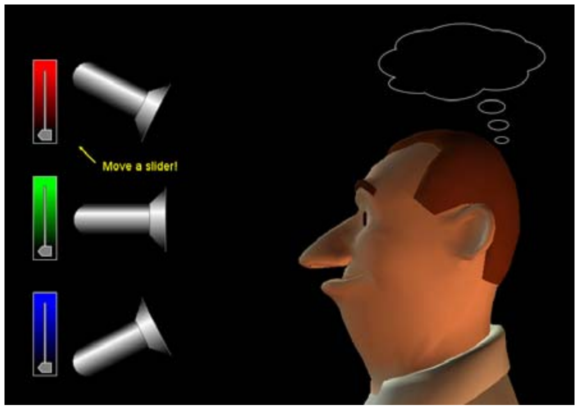
• light in 400-700 nm range interacts with a molecule (rhodopsin) in the rods and cones at the back of the eye (the retina)



• substances that absorb light in this region will appear colored

56

the perception of color depends on the wavelengths of light reaching the eye

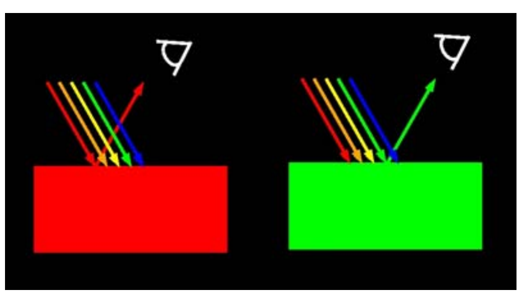


http://phet.colorado.edu/sims/color-vision/color-vision_en.jnlp

57

color and absorption of light

- The color of an object arises from the wavelengths **reflected** by the object and entering the eye
- If the object is viewed in white light (as is usual) the color seen is the **complement of the wavelengths absorbed**



58

color and absorption of light, white light (R+G+B) incident
(table 19.16) (complementary colors)

TABLE 19.16

Approximate Relationship of Wavelength of Visible Light Absorbed to Color Observed

Absorbed Wavelength in nm (color)	Observed Color
400 (violet)	Greenish yellow
450 (blue)	Yellow
490 (blue-green)	Red
570 (yellow-green)	Violet
580 (yellow)	Dark blue
600 (orange)	Blue
650 (red)	Green

reflects

R + G + B

(R,G,B) primaries

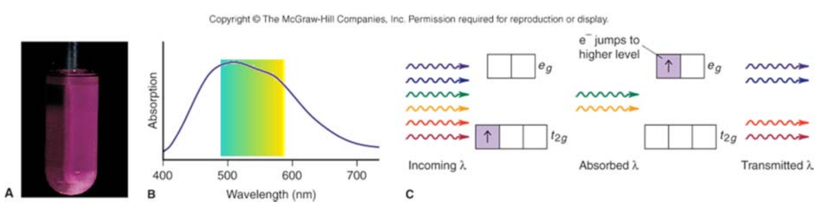
white=R+G+B
Y (yellow)=R+G
Cyan=G+B (blue-green)
Purple=R+B

know: **absorbs**	**appears**
no visible λ	**White**
B	**Yellow (R+G)**
Cyan (G+B)	**Red**
G	**Purple (R+B)**
Y (R+G)	**Blue**
R	**Green-Blue (cyan)**
R+G+B	**Black**

additive color mixing demo
subtractive color mixing demo

color and absorption of light
(Zumdahl fig 19.25, Silberberg fig. 23.20)

$[Ti(H_2O)_6]^{3+}$ d^1



absorbs green-yellow   appears purple

61

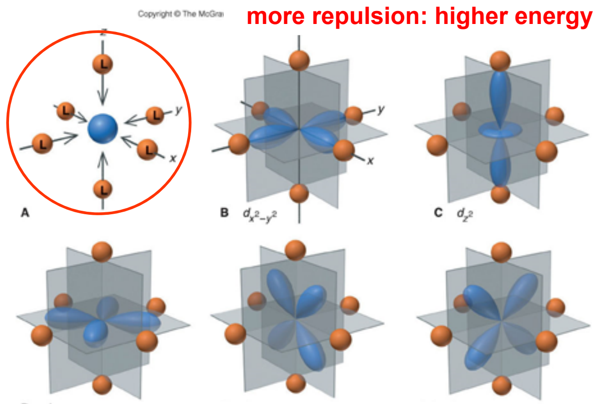
colored transition metal complexes- glazes

$Ni(NH_3)_6Br_2$ **$CoCl_2 \cdot 6H_2O$** **$NiSO_4 \cdot 6H_2O$**

http://woelen.scheikunde.net/science/chem/elem/metalsalts.jpg

62

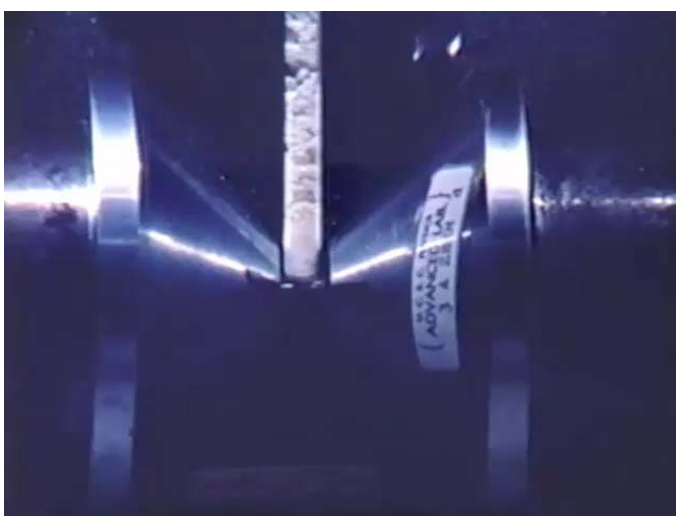
*metal ion d-obitals in **octahedral** complex*
(Silberberg fig. 23.17; Zumdahl fig. 19.21)



http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/Jmol/CrystalField/CFT_OrbsOctahedral_java.html(java)

63

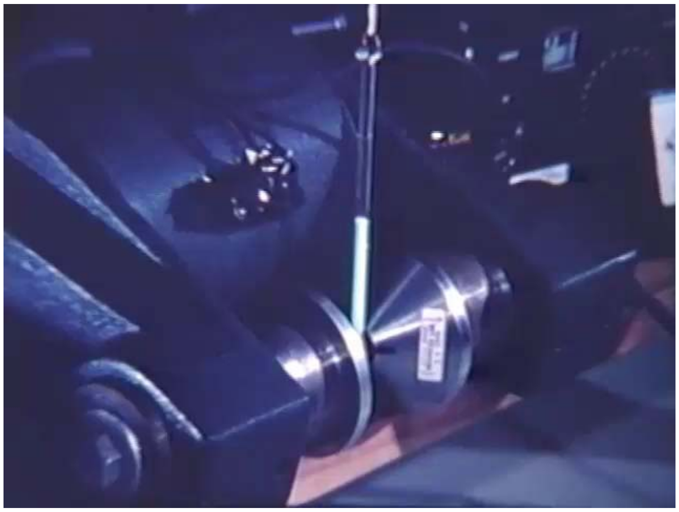
diamagnetism



open video in browser

64

paramagnetism

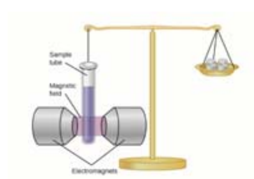


open video in browser

65

Gouy balance to measure magnetic properties

the Gouy (not the gooey !!) Balance

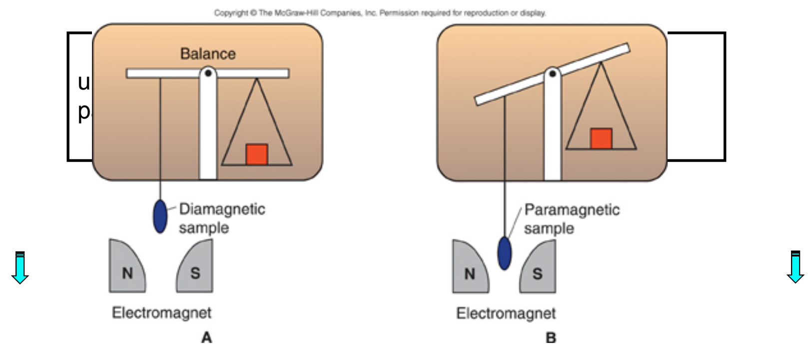


Louis Georges Gouy (1854-1926)

66

paramagnetism vs diamagnetism (Gouy balance)

diamagnetic paramagnetic



strength of paramagnetism depends on number of unpaired electrons

67

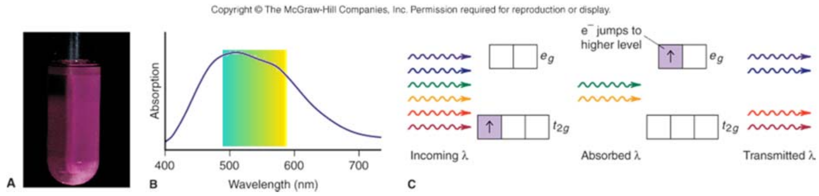
color

Color in octahedral complex ions arises from $t_{2g} \rightarrow e_g$ electronic transitions (excitations) that have energies corresponding to photons in the visible wavelengths.

68

color and absorption of light
(Zumdahl fig 19.25, Silberberg fig. 23.20)

$[Ti(H_2O)_6]^{3+}$ d^1



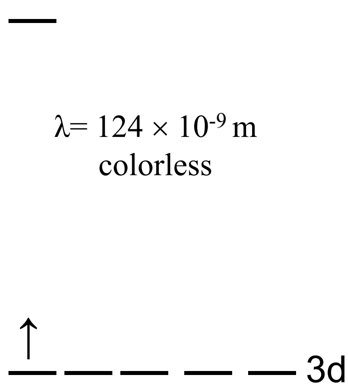
absorbs green-yellow appears purple

69

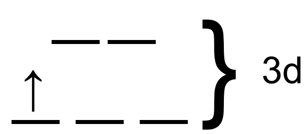
so ……

λ= 124 × 10⁻⁹ m
colorless

λ≈510 × 10⁻⁹ m
appears purple



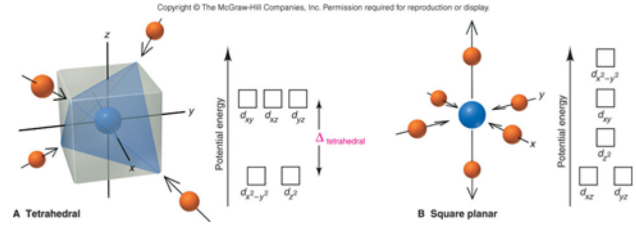
Ti^{3+} (g) d^1



$[Ti(H_2O)_6]^{3+}$ d^1

70

~~d-orbital energies for tetrahedral and square planar geometries (fig. 19.28,19.29)~~ (don't fret)



will not be on exams

71

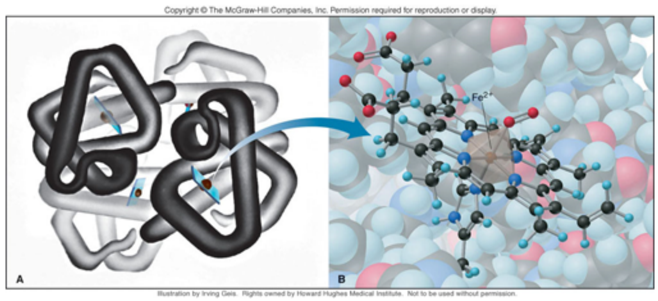
~~transition metals in biology (Zumdahl table 19.8, silberberg Table B23.1)~~ (don't fret)

Table B23.1 Some Transition Metal Trace Elements in Humans

Element	Biomolecule Containing Element	Function of Biomolecule
Vanadium	Protein (?)	Redox couple in fat metabolism (?)
Chromium	Glucose tolerance factor	Glucose utilization
Manganese	Isocitrate dehydrogenase	Cell respiration
Iron	Hemoglobin and myoglobin	Oxygen transport
	Cytochrome *c*	Cell respiration; ATP formation
	Catalase	Decomposition of H_2O_2
Cobalt	Cobalamin (vitamin B_{12})	Development of red blood cells
Copper	Ceruloplasmin	Hemoglobin synthesis
	Cytochrome oxidase	Cell respiration; ATP formation
Zinc	Carbonic anhydrase	Elimination of CO_2
	Carboxypeptidase A	Protein digestion
	Alcohol dehydrogenase	Metabolism of ethanol

72

transition metal complexes in biology



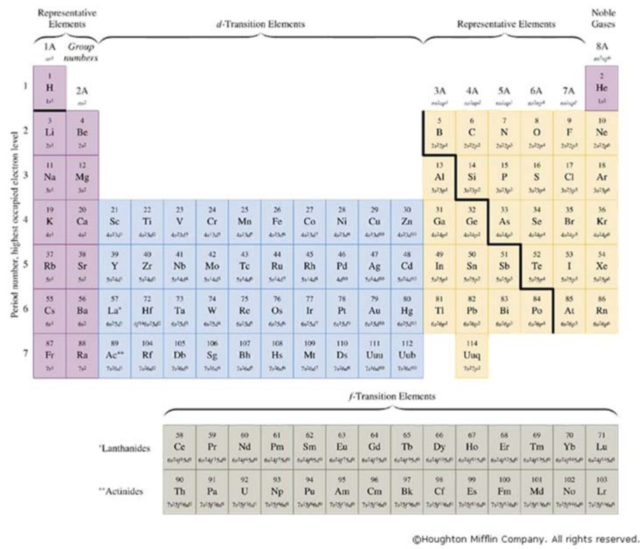
oxyheme deoxyheme

73

END

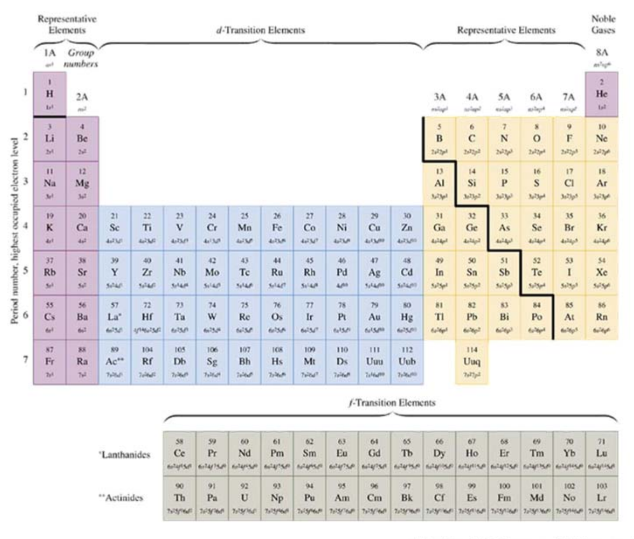
74

Zumdahl figure 12.29



75

Zumdahl figure 12.29



76

colored transition metal complexes- glazes

$Ni(NH_3)_6Br_2$

$CoCl_2 \cdot 6H_2O$

$NiSO_4 \cdot 6H_2O$

http://woelen.scheikunde.net/science/chem/elem/metalsalts.jpg

77