

Lectures 13-14 Coordination Complexes Lectures

Chemistry 1B, Fall 2013

Chemistry 1B
Fall 2013
Lectures 13-14

Coordination Chemistry

1

LISTEN UP!!!

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

2

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) →

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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

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simple example (figure on p. 942)

$[\text{Co}(\text{NH}_3)_6] \text{Cl}_3 (\text{s})$ salt of complex ion

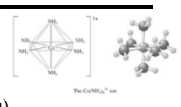
$[\text{Co}(\text{NH}_3)_6] \text{Cl}_3 (\text{s}) + \text{H}_2\text{O} \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+} (\text{aq}) + 3\text{Cl}^- (\text{aq})$

$[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ion denoted by []'s

6 NH_3 ligands

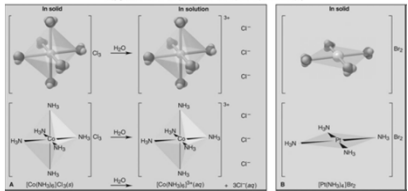
metal ion

3 Cl^- counter ions



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figure 23.9 (Silberberg)



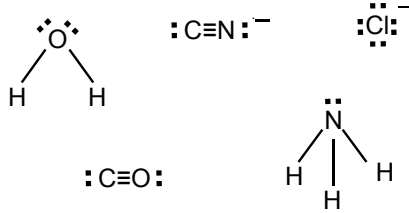
$[\text{Co}(\text{NH}_3)_6]^{3+} \Rightarrow$ octahedral

$[\text{Ni}(\text{CN})_4]^{2-} \Rightarrow$ square planar

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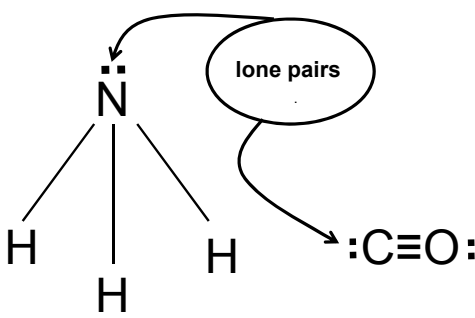
examples of common 'simple' ligands

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



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what is common structural feature of ligands



10

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

Lewis acid

Lewis base

ligand metal

$\text{L}:$ M^{+n}

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

Lewis base Lewis acid

ligand metal


$\text{L}:\text{M}^{+n}$

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coordinate covalent bonding

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

 coordination number = 6

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

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Table 23.6 Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape	Examples
2	Linear	$[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)]^+$, $[\text{AuCl}_2]^-$
4	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PtCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral	$[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CoCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
6	Octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$

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ligands (Table 23.7 Silberberg) [Table 19.13 Zumdahl]

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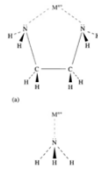
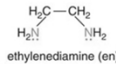
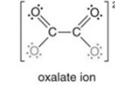
Table 23.7 Some Common Ligands in Coordination Compounds

Ligand Type	Examples
Monodentate	H_2O water NH_3 ammonia F^- fluoride ion Cl^- chloride ion $[\text{C}\equiv\text{N}]^-$ cyanide ion $[\text{S}\equiv\text{C}\equiv\text{N}]^-$ thiocyanate ion $[\text{C}\equiv\text{N}]^-$ or $[\text{N}\equiv\text{C}]^-$ $[\text{H}-\text{O}^-]$ hydroxide ion $[\text{O}^--\text{N}=\text{O}]^-$ nitrite ion

monodentate

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

Bidentate




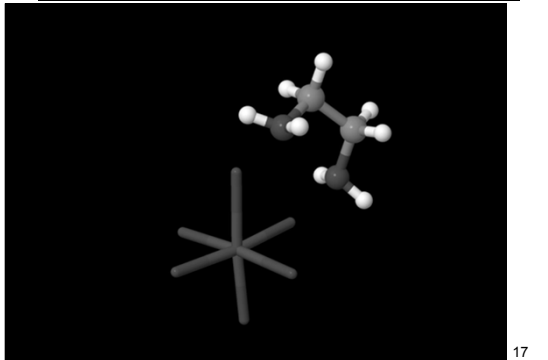
 ethylenediamine (en)
 oxalate ion

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.

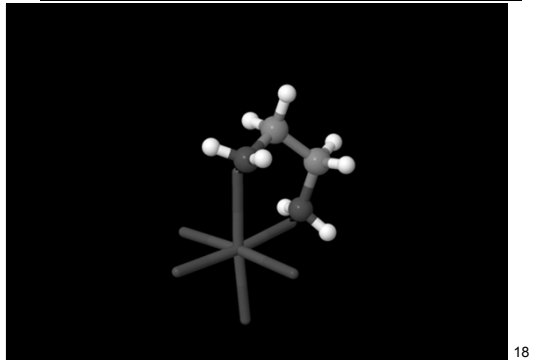
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ethylene diamine bidentate ligand



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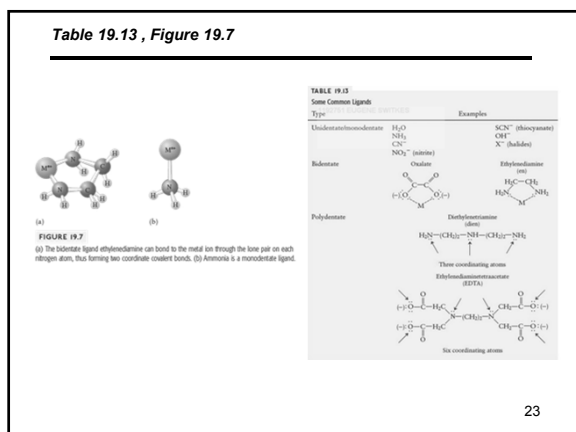
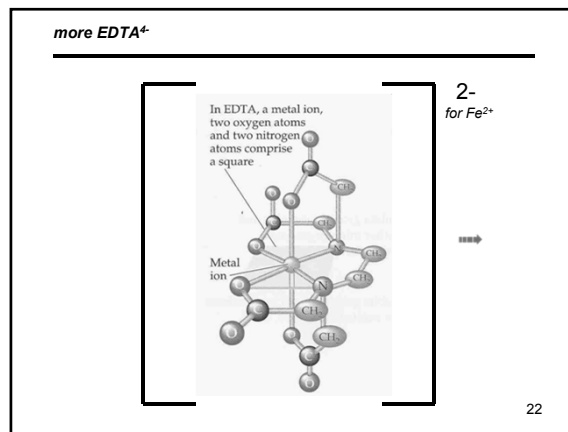
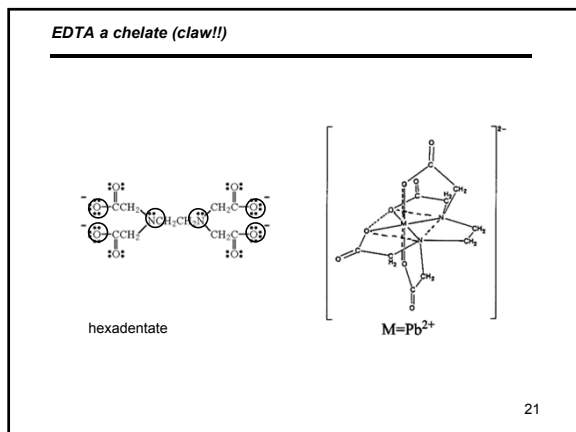
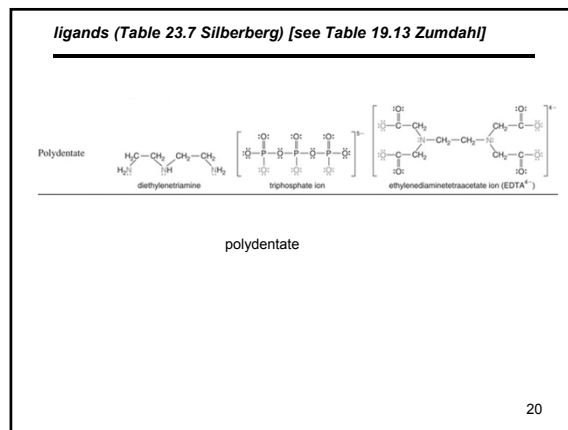
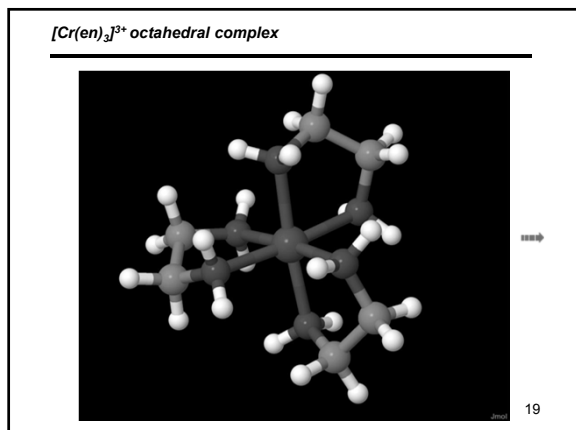
ethylene diamine bidentate ligand



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determining: num ligands charge oxidation state d-electrons

given [Co(NH₃)_n] Cl₃ is salt of octahedral complex

- coordination number=6 since octahedral
- n=6 since NH₃ is monodentate ligand
- 3⁺ charge on complex from counterion: 3 Cl⁻
- Co³⁺ oxidation state of metal from charge on complex and zero charge on NH₃ ligands
- d⁶ d-electrons from aufbau principle FOR CATIONS

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other examples

$K_3[Fe(CN)_6]$ octahedral

$[Co(en)_3]Cl_3$ octahedral

$Na_2[Ni(CN)_4]$ square planar



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

- General facts about transition metals
- Nomenclature
- Isomerism


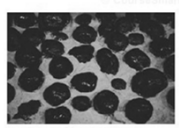


FIGURE 19.4
A bicycle with a titanium frame.



Manganese nodules on the sea floor.




FIGURE 19.15

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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

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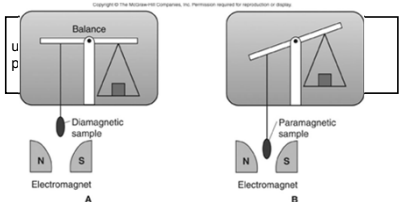
crystal field theory (pp 964-970)

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

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paramagnetism vs diamagnetism (Gouy balance)

diamagnetic paramagnetic



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Electromagnet A Electromagnet B

strength of paramagnetism depends on number of unpaired electrons

not now

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crystal field theory and color

- most electronic excitations in UV
($H 1s \rightarrow H 2p \lambda = 121 \times 10^{-9} \text{ m}$)
- $Co^{3+} [Ar]3d^6 \rightarrow Co^{3+} [Ar]3d^5 4s^1$ ($\lambda = 75.3 \times 10^{-9} \text{ m}$) **UV**
 $NH_3 \rightarrow NH_3^*$ (excited state) ($\lambda = 216 \times 10^{-9} \text{ m}$) **UV**

but in coordination complex

- $[Co(NH_3)_6]^{3+} \rightarrow$ excited state* ($\lambda = 430 \times 10^{-9} \text{ m}$, absorbs 'indigo')

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

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crystal field theory and magnetic properties

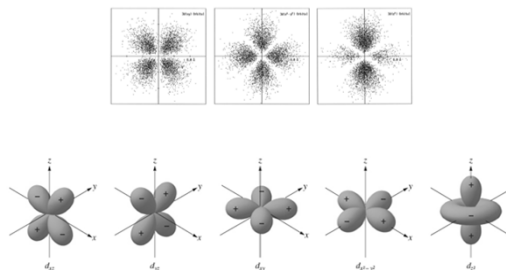
$[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic

but

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

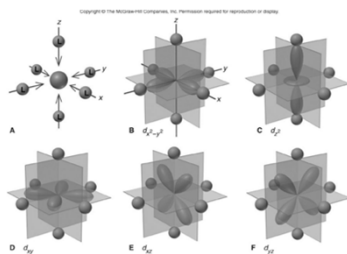
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remember atomic d-orbitals (figure 12.21)



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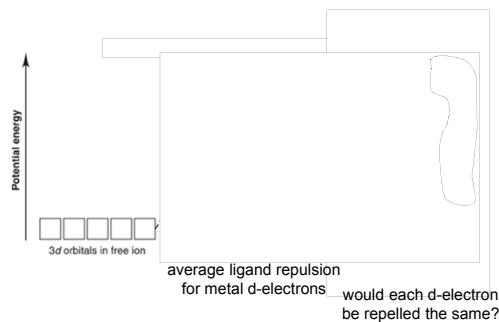
metal ion d-orbitals in octahedral complex (Silberberg fig. 23.17; Zumdahl fig. 19.21)



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

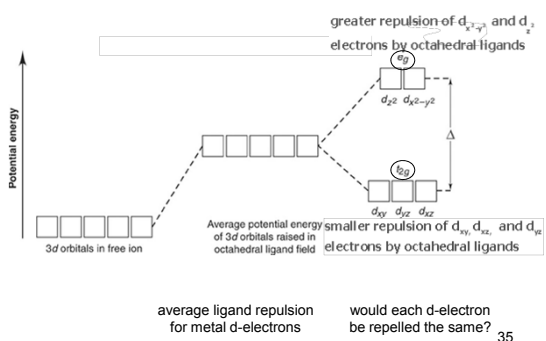
33

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



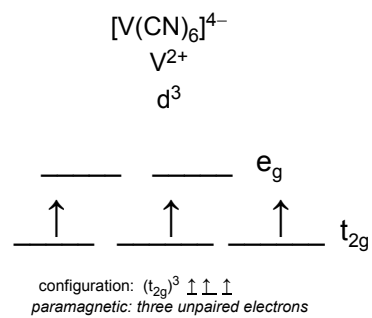
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what happens to energies of d-orbitals when ligands bind to metal ion? (fig 23.18)



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



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

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ vs $[\text{Cr}(\text{CN})_6]^{4-}$
 Cr^{2+} Cr^{2+}
 d^4 d^4

$\begin{array}{c} \text{?} \\ \text{---} \\ \uparrow \text{?} \end{array}$
 $\begin{array}{c} \text{---} \\ \uparrow \end{array}$
 $\begin{array}{c} \text{---} \\ \uparrow \end{array}$
 $\begin{array}{c} e_g \\ \text{---} \\ \uparrow \end{array}$
 $\begin{array}{c} t_{2g} \\ \text{---} \\ \uparrow \end{array}$

where does electron 4th go ?

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

d^4 Weak-field ligands Strong-field ligands d^4

$\begin{array}{c} e_g \\ \uparrow \end{array}$
 $\begin{array}{c} t_{2g} \\ \uparrow \uparrow \uparrow \end{array}$
 Δ
 $\begin{array}{c} e_g \\ \uparrow \downarrow \end{array}$
 $\begin{array}{c} t_{2g} \\ \uparrow \uparrow \uparrow \end{array}$
 Δ

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ $[\text{Cr}(\text{CN})_6]^{4-}$

$(E_{\text{pairing}}) > \Delta$ $\Delta > (E_{\text{pairing}})$
 small Δ favors filling large Δ favors filling
 maximum unpaired spins lowest orbitals first

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$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ vs $[\text{Cr}(\text{CN})_6]^{4-}$

- $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, d^4 , weak-field \equiv high spin, 4 unpaired electrons, paramagnetic
- $[\text{Cr}(\text{CN})_6]^{4-}$, d^4 , strong-field \equiv low spin, 2 unpaired electrons, paramagnetic

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

small Δ High spin: weak-field ligand Low spin: strong-field ligand large Δ

d^4 $\begin{array}{c} \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \\ \square \end{array}$
 $\begin{array}{c} \uparrow \uparrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$

d^5 $\begin{array}{c} \uparrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$
 $\begin{array}{c} \uparrow \uparrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$

d^6 $\begin{array}{c} \uparrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$
 paramagnetic $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$ diamagnetic

d^7 $\begin{array}{c} \uparrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$
 $\begin{array}{c} \uparrow \uparrow \uparrow \\ \square \end{array}$ $\begin{array}{c} \uparrow \downarrow \uparrow \\ \square \end{array}$

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other examples (do in section)

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, d^6 , weak field, 4 unpaired e's, paramagnetic

$[\text{Fe}(\text{CN})_6]^{4-}$, d^6 , strong field, 0 unpaired e's, diamagnetic

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

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$\text{I}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{SCN}^- < \text{NH}_3 < \text{en} < \text{NO}_2^- < \text{CN}^- < \text{CO}$

WEAKER FIELD STRONGER FIELD

SMALLER Δ LARGER Δ

LONGER λ SHORTER λ

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

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crystal field theory (pp 959-955)

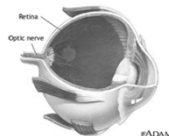
- How are the magnetic properties of transition metal complexes related to the shape of d-orbitals?
- Why are transition metal complexes colored?

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why are some molecules colored? (spectroscopy lectures later)

human vision and chemistry LATER in spectroscopy not now

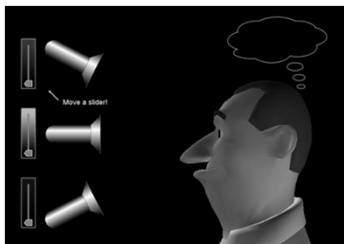
- light in 400-700 nm range interacts with a molecule (rhodopsin) in the rods and cones at the back of the eye (the retina)



- substances that absorb light in this region will appear colored

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



http://phet.colorado.edu/sims/color-vision/color-vision_en.in1p

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color and absorption of light

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



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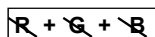
color and absorption of light, white light (R+G+B) incident (table 19.16)

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

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

additive color mixing demo

subtractive color mixing demo

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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.

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

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} d^1$

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A B C

absorbs green-yellow appears purple

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so

$\lambda = 11.4 \times 10^{-9} \text{ m}$
colorless

$\lambda \approx 510 \times 10^{-9} \text{ m}$
appears purple

$\text{Ti}^{3+} (\text{g}) d^1$ $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} d^1$

3d 3d

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d-orbital energies for tetrahedral and square planar geometries
(fig. 19.26, 19.29)

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A Tetrahedral B Square planar

will not be on exams

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

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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 Cytochrome c Catalase	Oxygen transport Cell respiration; ATP formation Decomposition of H_2O_2
Cobalt	Cobalamin (vitamin B_{12})	Development of red blood cells
Copper	Ceruloplasmin Cytochrome oxidase	Hemoglobin synthesis Cell respiration; ATP formation
Zinc	Carbonic anhydrase Carboxypeptidase A Alcohol dehydrogenase	Elimination of CO_2 Protein digestion Metabolism of ethanol

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transition metal complexes in biology

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A B

oxyheme deoxyheme

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END

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Zumdahl figure 12.29

Periodic table showing the d-block (Transition Elements), f-block (Lanthanides and Actinides), and p-block (Representative Elements). The d-block is shaded in light blue, the f-block in light green, and the p-block in light purple. Noble gases are in the far right column.

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Zumdahl figure 12.29

Periodic table showing the d-block (Transition Elements), f-block (Lanthanides and Actinides), and p-block (Representative Elements). The d-block is shaded in light blue, the f-block in light green, and the p-block in light purple. Noble gases are in the far right column.

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colored transition metal complexes- glazes

Three small vials containing colored powders representing transition metal complexes:

- $\text{Ni}(\text{NH}_3)_6\text{Br}_2$
- $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$
- $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

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

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d-Orbitals and ligand Interaction (octahedral field)

Diagram illustrating the interaction of d-orbitals with ligands in an octahedral field. The central metal ion is Ni^{2+} with a $3d^8$ configuration. The ligands are NH_3 and Cl^- . The diagram shows the splitting of the five degenerate d-orbitals into two higher-energy e_g orbitals (pointing directly at the axes) and three lower-energy t_{2g} orbitals (not pointing directly at the axes). The energy difference is labeled as Δ_o .

$\text{Ni}(\text{NH}_3)_6\text{Cl}_2 \xrightarrow{\text{H}_2\text{O}} [\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq})$

$\text{Ni}^{2+} [\text{Ar}]3d^8$

d-orbitals pointing directly at axis are affected most by electrostatic interaction

d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

ibchem.com/IB/libfiles/periodicity/per_pp1/Crystal_field_theory.ppt

absorption of visible light in octahedral transition metal complexes

Energy level diagram for $[\text{Ni}(\text{NH}_3)_6]^{2+}$. The ground state is $t_{2g}^6 e_g^2$ and the excited state is $t_{2g}^5 e_g^3$. An arrow indicates the absorption of light causing an electronic transition from the ground state to the excited state.

- 3d orbitals all have same energy in $\text{Ni}^{2+}(\text{g})$
- presence of 6NH_3 cause "splitting of the energies of the 3d-orbitals into two levels in $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- visible light causes electronic transitions between the two levels resulting in 'colored' transition metal complexes

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absorption of visible light in octahedral transition metal complexes

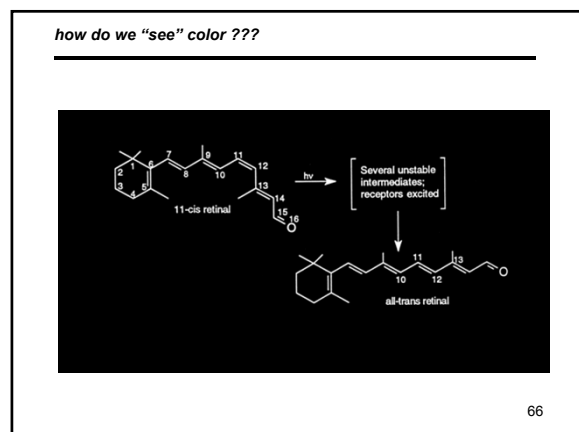
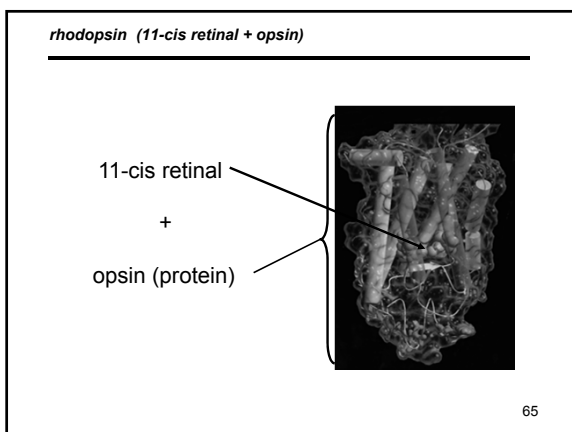
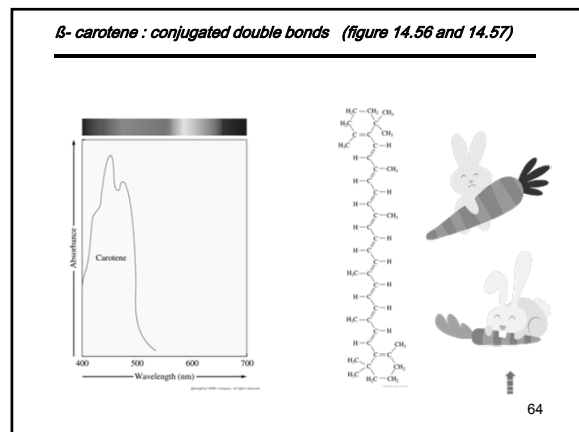
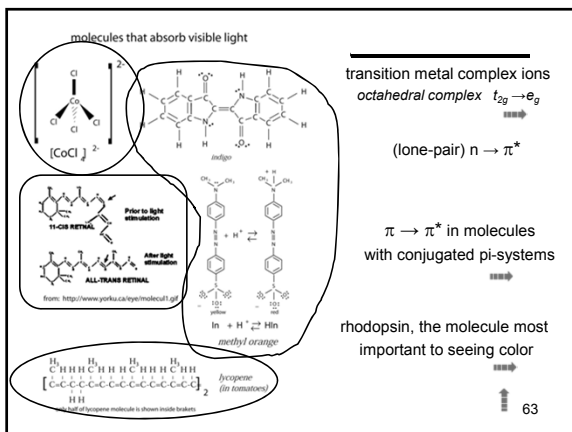
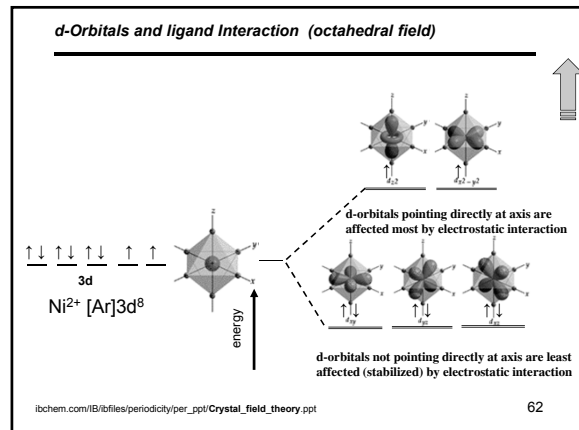
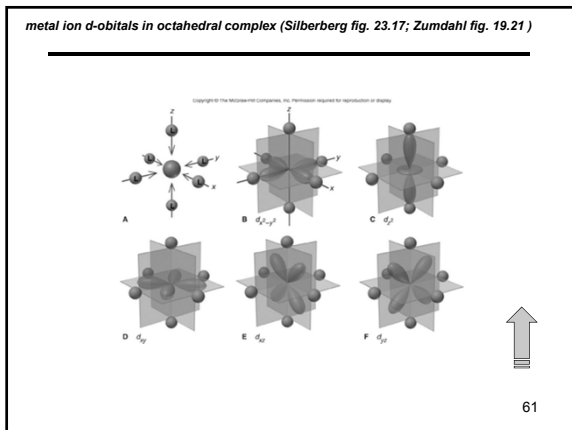
Energy level diagram for $[\text{Ni}(\text{NH}_3)_6]^{2+}$. The ground state is $t_{2g}^6 e_g^2$ and the excited state is $t_{2g}^5 e_g^3$. An arrow indicates the absorption of light causing an electronic transition from the ground state to the excited state.

- 3d orbitals all have same energy in $\text{Ni}^{2+}(\text{g})$
- presence of 6NH_3 cause "splitting of the energies of the 3d-orbitals into two levels in $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- visible light causes electronic transitions between the two levels resulting in 'colored' transition metal complexes

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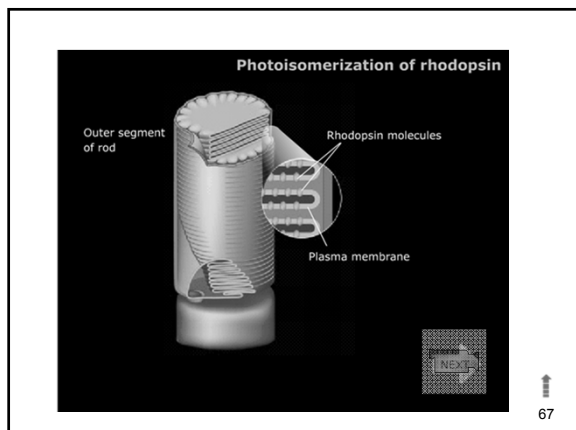
Lectures 13-14 Coordination Complexes Lectures

Chemistry 1B, Fall 2013



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paramagnetism

- each electron behaves as tiny magnet \uparrow or \downarrow (Stern-Gerlach experiment)
- when electrons in a molecule have paired spins the individual magnets cancel one another $\uparrow\downarrow$
- when an atom or molecule has **unpaired** electrons there is a resulting "net-magnetic moment" $\uparrow\uparrow\uparrow$
- atoms with unpaired electrons are attracted by an [inhomogeneous] magnetic field
- atoms with unpaired electrons are **paramagnetic**

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diamagnetism (DO FRET)

- diamagnetism is much weaker than paramagnetism
- in paramagnetic molecules there is some diamagnetism but it is overwhelmed by stronger paramagnetism
- atoms/molecules with **completely paired electrons** in closed-shells are **diamagnetic and are pushed out of a [inhomogeneous] magnetic field**

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diamagnetism (don't fret)

- diamagnetism arises from the circulating (orbiting) motion of closed-shell electrons
- an external magnet "speeds-up" the motion of electrons in one orbits (say p_{+1}) and "slows down" the motion of the electrons in another orbit (say p_{-1})
- this imbalance creates a magnetic field in the atom or molecule in a direction which pushes the sample out of the magnet

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the floating frog

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052 SCIENCE NEWS, VOL. 152 DECEMBER 6, 1997

Floating Frogs

Magnets help living organisms defy gravity

By CORINNA WU

Floating Frogs
by Corinna Wu

(This was demonstrated on both Dan Rather's CBS News and CNN in April of 1997)

Asked to think of an animal that can fly, most people don't picture a frog. Nonetheless, in April 1997, a team of British and Dutch researchers announced success in facilitating a live frog fly using a powerful magnet. According to one of the human observers, the frog emerged from the flight unburned and "happily joined" his fellow frogs in a biology department.

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the magnet

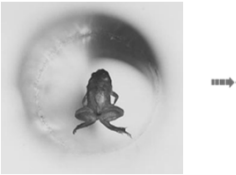
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Lectures 13-14 Coordination Complexes Lectures

Chemistry 1B, Fall 2013

the frog


The Frog That Learned to Fly (Molecular Magnetism and Levitation)



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the frog's OK !!!

researchers announced success in levitating a live frog by using a powerful magnet. According to one of the human observers, the frog emerged from the flight unharmed and "happily joined" his fellow frogs in a biology department.

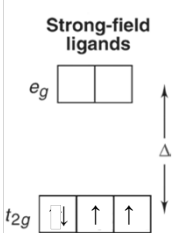


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strong and weak field ligands: lowest orbitals vs unpaired spins
 Δ vs (E_{pairing}) (Silberberg fig 23.18)

d^4 d^4

Strong-field ligands



e_g

t_{2g}

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

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

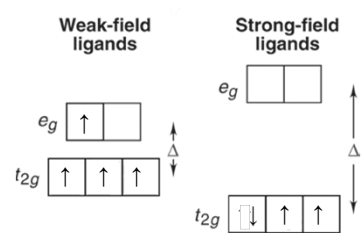
E_{pairing}
small Δ favors filling maximum unpaired spins

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

d^4 d^4

Weak-field ligands **Strong-field ligands**



e_g

t_{2g}

$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ $[\text{Cr}(\text{CN})_6]^{4-}$

$(E_{\text{pairing}}) > \Delta$ $\Delta > (E_{\text{pairing}})$
small Δ favors filling maximum unpaired spins large Δ favors filling lowest orbitals first

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