

Topics 17-18 Coordination Complexes

Chemistry 1B-AL , Fall 2016

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

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

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

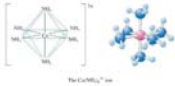
$[\text{Co}(\text{NH}_3)_6]^{3+} (\text{aq}) + 3\text{Cl}^- (\text{aq})$

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

6 NH_3 ligands

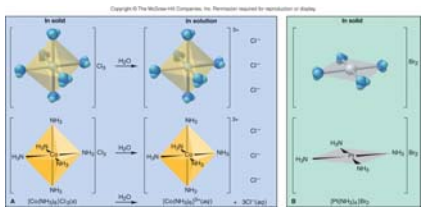
metal ion

3Cl^- counter ions



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figure 23.9 (Silberberg)



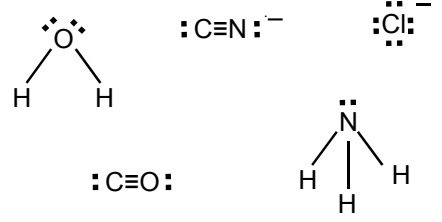
$[\text{Co}(\text{NH}_3)_6]^{3+} \Rightarrow$ octahedral

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

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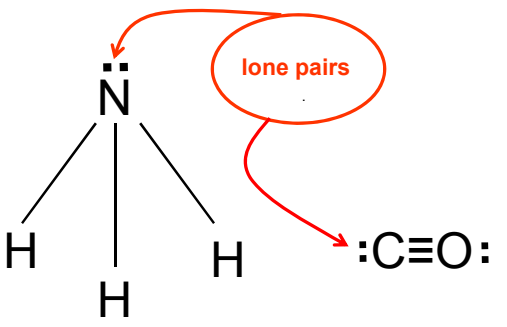
examples of common 'simple' ligands

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 | $[\text{CoCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$ |
| 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 | $[\text{Co}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CoCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$ |
| 6 | Octahedral | $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{4-}$, $[\text{Co}(\text{en})_3]^{3+}$ |

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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, $[\text{O}^- - \text{H}]^-$ hydroxide ion, $[\text{O}^- - \text{N} = \text{O}]^-$ nitrite ion |

monodentate

atom forming coordinate covalent bond indicated in BLUE

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

Bidentate

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ethylenediamine (en)

bidentate

oxalate ion

atoms forming coordinate covalent bonds indicated in BLUE

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

M^+

nitrite ion

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ethylene diamine **bidentate** ligand

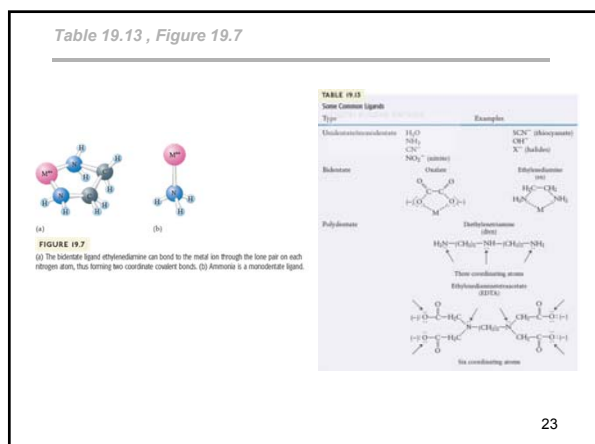
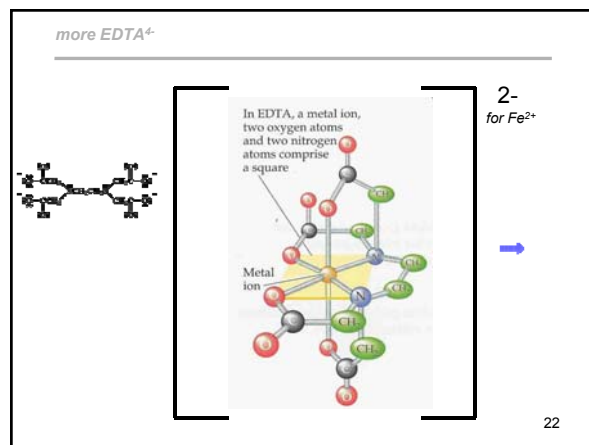
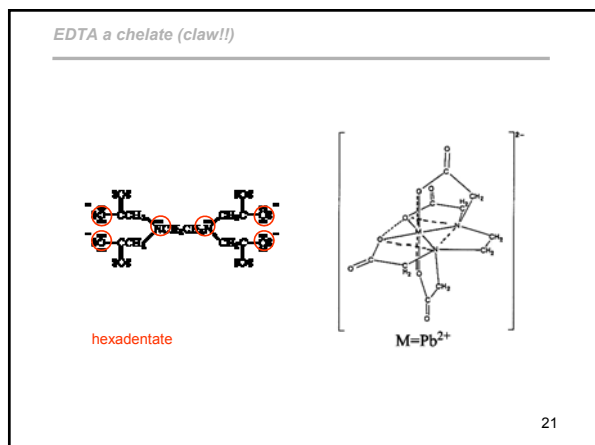
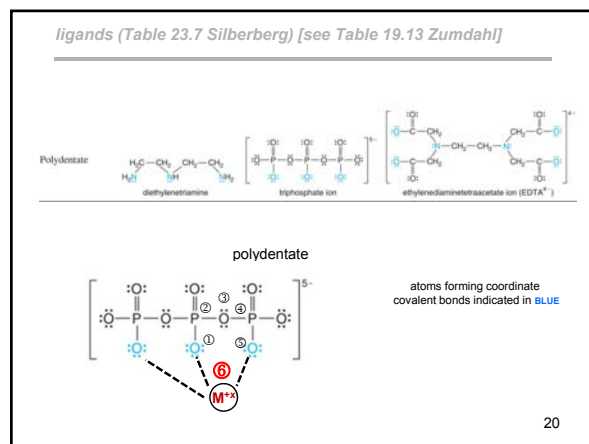
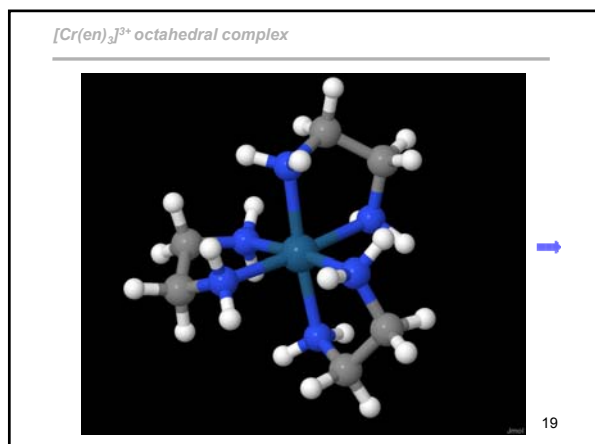
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ethylene diamine **bidentate** ligand

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determining: num ligands charge oxidation state d-electrons

given $[Co(NH_3)_n]Cl_3$ 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 963-964, 965-963)~~ (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^2 four square planar hybrids

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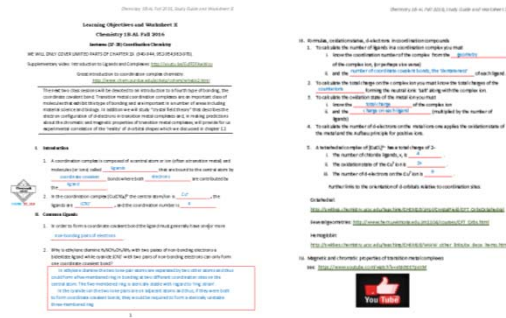
Crystal Field Theory of
Coordination Complexes

magnetic properties
and
pretty colors

(pp 964-970)


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have covered worksheet 10 I-III



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




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recommended !!!!


IV. Magnetic and chromatic properties of transition metal complexes
 see: <https://www.youtube.com/watch?v=xNKRSE7pxXM>



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basic aims of this video presentation

crystal-field theory of transition metal coordination complexes

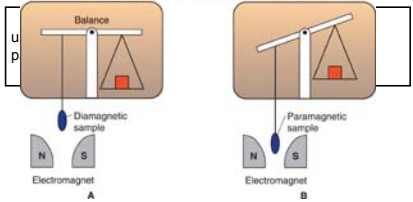
"reality" of the shapes of d-orbitals 

- 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?

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paramagnetism vs diamagnetism (Gouy balance) 

diamagnetic paramagnetic



strength of paramagnetism depends on number of unpaired electrons

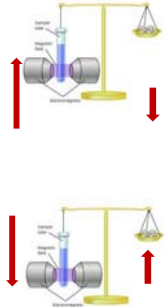
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crystal field theory and magnetic properties $[\text{Co}(\text{NH}_3)_6]^{3+}$ vs $[\text{Co}(\text{F})_6]^{3-}$

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

but


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



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crystal field theory and color

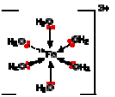

- most electronic excitations in UV ($\text{H } 1s \rightarrow \text{H } 2p \lambda=121 \text{ nm}$)
- $\text{Co}^{3+} [\text{Ar}]3d^6 \rightarrow \text{Co}^{3+} [\text{Ar}]3d^5 4s^1$ ($\lambda=75.3 \text{ nm}$) **UV**
 $\text{NH}_3 \rightarrow \text{NH}_3^*$ (excited state) ($\lambda=216 \text{ nm}$) **UV**
 Co^{3+} and NH_3 are colorless !!!
but in coordination complex
- $[\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow$ excited state* ($\lambda=430 \text{ nm}$, absorbs 'indigo')



$[\text{NH}_3)_6]^{3+}$ appears yellow-orange !!

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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. 

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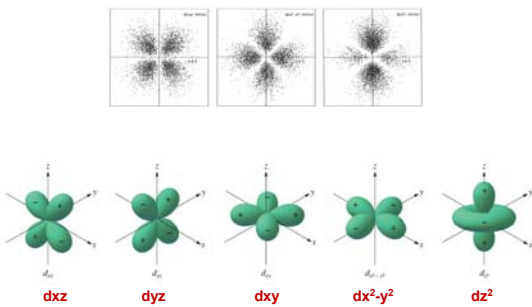
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limiting the playing field 

- 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)

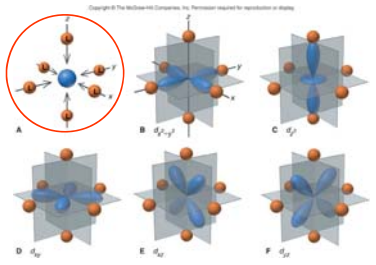
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remember atomic d-orbitals (figure 12.21)



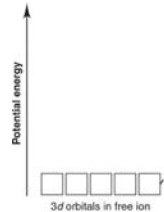
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metal ion d-orbitals in octahedral complex
(Silberberg fig. 23.17; Zumdahl fig. 19.21)



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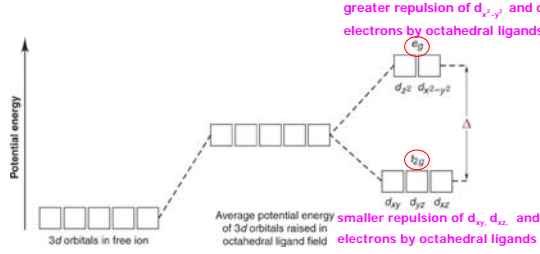
what happens to energies of d-orbitals when ligands bind to metal ion? (fig 23.18)



average ligand repulsion for metal d-electrons would each d-electron be repelled the same?

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



greater repulsion of d_{xz} , d_{yz} , and d_{xy} electrons by octahedral ligands

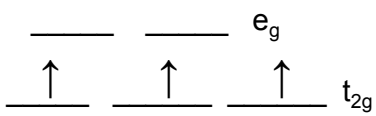
smaller repulsion of $d_{x^2-y^2}$, d_{z^2} , and d_{xy} electrons by octahedral ligands

average ligand repulsion for metal d-electrons would each d-electron be repelled the same?

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

$[V(CN)_6]^{4-}$
 V^{2+}
 d^3



configuration: $(t_{2g})^3 \uparrow \uparrow \uparrow$
paramagnetic: three unpaired electrons

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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+} d^4 vs Cr^{2+} d^4

$\begin{array}{c} \text{?} \\ \text{---} \\ \uparrow \text{?} \end{array} \quad \begin{array}{c} \text{---} \\ \uparrow \end{array} \quad \begin{array}{c} \text{---} \\ \uparrow \end{array} \quad \begin{array}{c} \text{---} \\ \uparrow \end{array} \quad \begin{array}{c} \text{---} \\ \uparrow \end{array} \quad \begin{array}{c} \text{---} \\ \uparrow \end{array}$

e_g t_{2g}

where does electron 4th go?

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

$\begin{array}{c} \uparrow \\ \uparrow \\ \uparrow \end{array} \quad \begin{array}{c} \uparrow \\ \uparrow \\ \uparrow \end{array} \quad \begin{array}{c} \uparrow \\ \uparrow \\ \uparrow \end{array} \quad \begin{array}{c} \uparrow \\ \uparrow \\ \uparrow \end{array}$

e_g t_{2g}

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

$\uparrow \downarrow \quad \uparrow \quad \uparrow$

e_g t_{2g}

costs E_{pairing} but not Δ

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

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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** d^4

e_g t_{2g}

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

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

Strong-field ligands d^4

e_g t_{2g}

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

$\Delta > (E_{\text{pairing}})$
large Δ favors filling 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,
 $\uparrow \uparrow \uparrow \uparrow$ $t_{2g}^3 e_g^1$
 4 unpaired electrons, paramagnetic
- $[\text{Cr}(\text{CN})_6]^{4-}$, d^4 , strong-field \equiv low spin,
 $\uparrow \downarrow \uparrow \uparrow$ t_{2g}^4
 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

d^5

d^6

d^7

paramagnetic diamagnetic

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

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

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
 if 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?

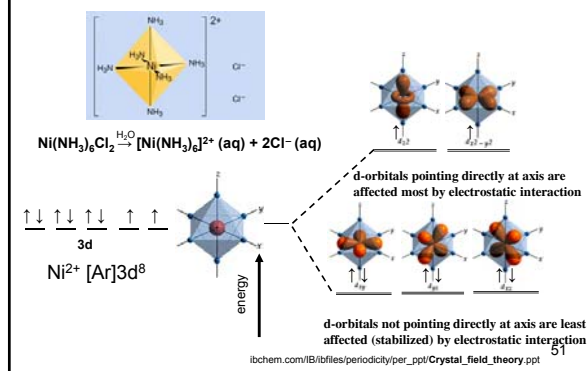
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color

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.

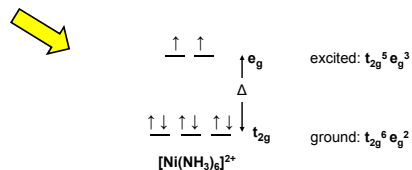
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d-Orbitals and ligand Interaction (octahedral field)



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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 !!]

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Perception of
the Color of Objects

an addendum to
Crystal Field Theory

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absorption of visible light in octahedral transition metal complexes

excited: $t_{2g}^5 e_g^3$
ground: $t_{2g}^6 e_g^2$
 $[Ni(NH_3)_6]^{2+}$

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

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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.inlp

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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**

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

| 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 no visible λ appears 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

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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

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all done

Hold your hands up and twist them, like you're brushing everything away. All done or finished. Let's see you sign it!

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colored transition metal complexes- glazes

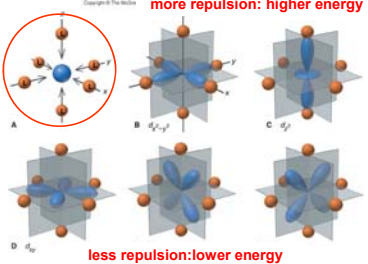


$\text{Ni}(\text{NH}_3)_6\text{Br}_2$ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

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

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



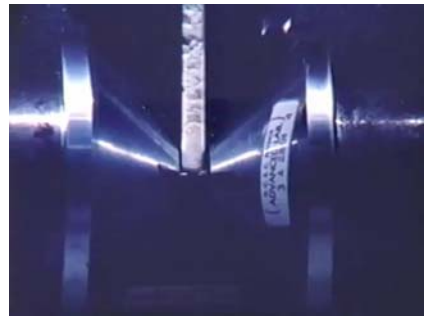
more repulsion: higher energy

less repulsion: lower energy

[http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/mol/CrystalField/CFT_OrbsOctahedral_java.html\(java\)](http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/mol/CrystalField/CFT_OrbsOctahedral_java.html(java))

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diamagnetism



[open video in browser](#)

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paramagnetism

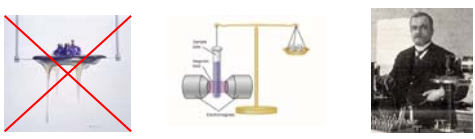


[open video in browser](#)

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Gouy balance to measure magnetic properties

the Gouy (not the gooey !!) Balance



Louis Georges Gouy
(1854-1926)

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paramagnetism vs diamagnetism (Gouy balance)

diamagnetic paramagnetic

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Strength of paramagnetism depends on number of unpaired electrons

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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

absorbs green-yellow appears purple

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SO

$\lambda = 124 \times 10^{-9} \text{ m}$
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

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~~d-orbital energies for tetrahedral and square planar geometries (fig. 19.20, 19.29) (don't fret)~~

will not be on exams

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~~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 |

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transition metal complexes in biology

oxyheme deoxyheme →

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END

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Zumdahl figure 12.29

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Zumdahl figure 12.29

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colored transition metal complexes- glazes

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

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

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