Chemistry 1B

Fall 2016

Topics Lectures 17-18

Coordination Chemistry

• WE WILL ONLY COVER LIMITED PARTS OF CHAPTER 19

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

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)

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

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

 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 a

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

simple example (figure on p. 942)

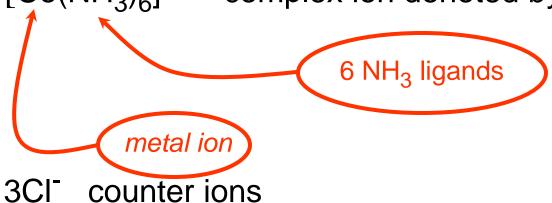
$$[Co(NH_3)_6]$$
 Cl_3 (s) salt of complex ion

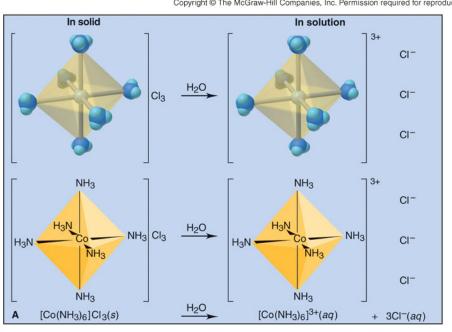
The Co(NH₃)₆³⁺ ion

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

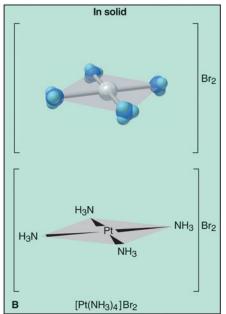
$$[Co(NH_3)_6]^{3+}(aq) + 3CI^{-}(aq)$$

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





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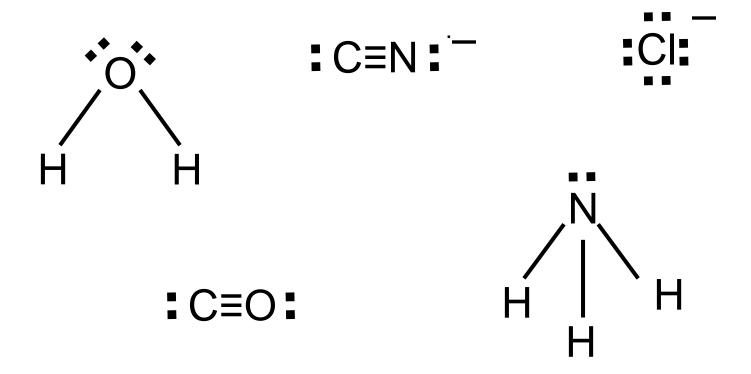


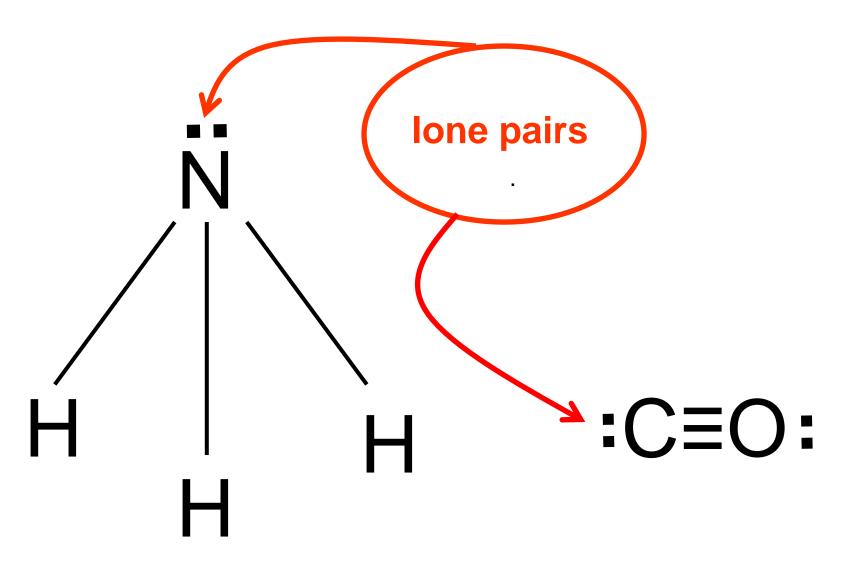
octahedral



square planar

 H_2O , NH_3 , CI^- , CO, CN^-





Lewis acid

Lewis base

ligand

metal

L:

M+n

Lewis base

ligand

Lewis acid

metal



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



coordination number =6

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

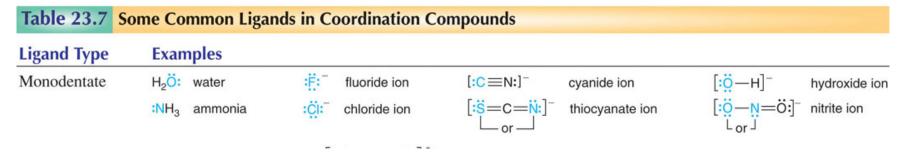
 Table 23.6
 Coordination Numbers and Shapes of Some Complex Ions
 Coordination Number Shape **Examples** $[CuCl_2]^-$, $[Ag(NH_3)_2]^+$, $[AuCl_2]^-$ Linear [Ni(CN)₄]²⁻, [PdCl₄]²⁻, [Pt(NH₃)₄]²⁺, [Cu(NH₃)₄]²⁺ Square planar $[Cu(CN)_4]^{3-}$, $[Zn(NH_3)_4]^{2+}$, $[CdCl_4]^{2-}$, $[MnCl_4]^{2-}$ Tetrahedral
$$\begin{split} &[\text{Ti}(\text{H}_2\text{O})_6]^{3^+}, [\text{V}(\text{CN})_6]^{4^-}, \\ &[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+, [\text{Mn}(\text{H}_2\text{O})_6]^{2^+}, \\ &[\text{FeCl}_6]^{3^-}, [\text{Co}(\text{en})_3]^{3^+} \end{split}$$
Octahedral

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ligands (Table 23.7 Silberberg) [Table 19.13 Zumdahl]

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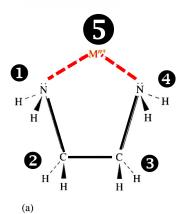


monodentate

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

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

Bidentate



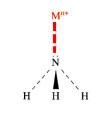
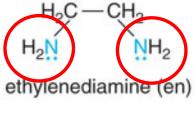


Figure 20.7 (a) The bidentate ligand ethylenediamine can bond to the metal ion through the lone pair on each nitrogen atom, thus forming two coordinate covalent bonds. (b) Ammonia is a monodentate ligand.

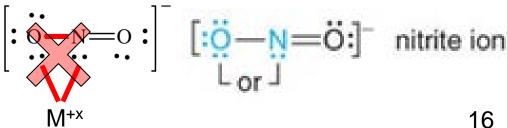
(b)



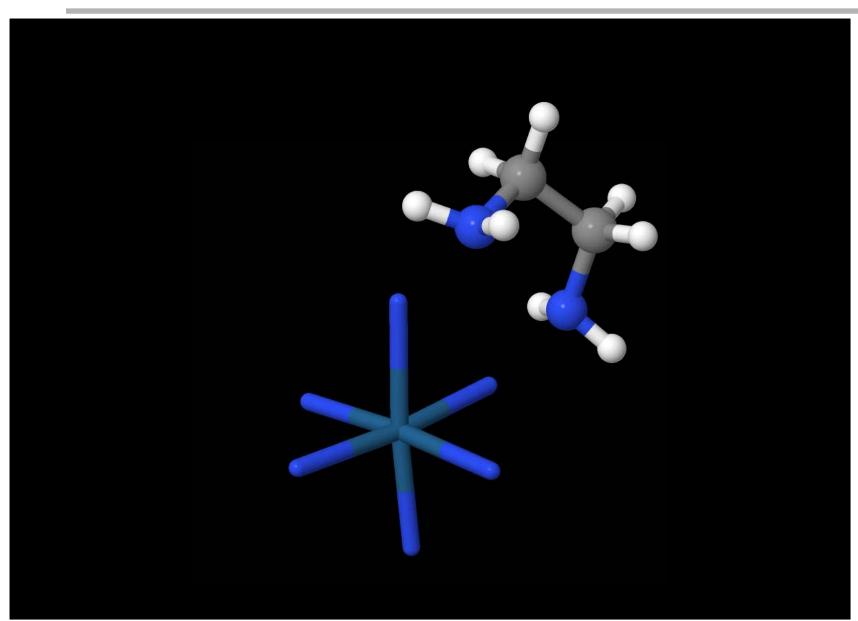


atoms forming coordinate covalent bonds indicated in **BLUE**

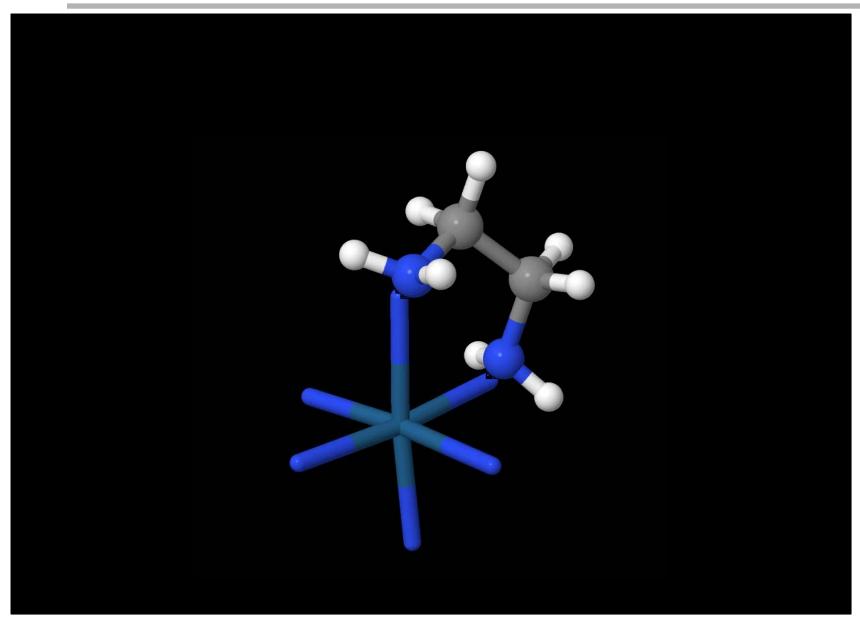
multi-dentate 5 or six membered ring with M⁺

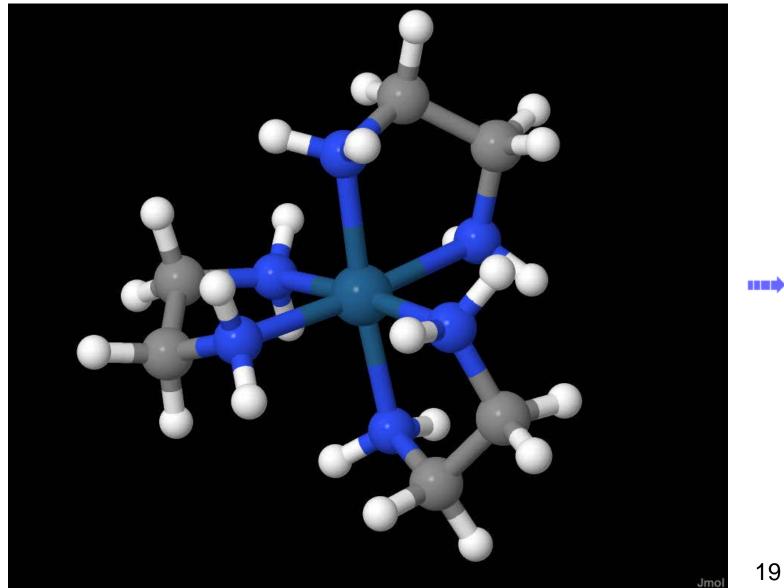


ethylene diamine bidentate ligand



ethylene diamine bidentate ligand

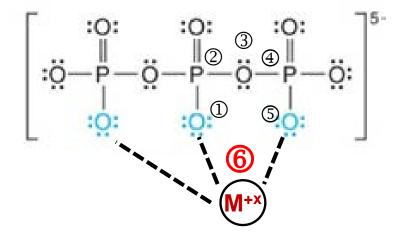




ligands (Table 23.7 Silberberg) [see Table 19.13 Zumdahl]

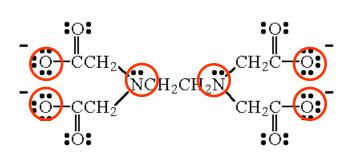
Polydentate
$$\begin{array}{c} \text{Polydentate} \\ \text{H}_2\text{C} - \text{CH}_2 \quad \text{CH}_2 - \text{CH}_2 \\ \text{H}_2\text{N} \quad \text{NH} \quad \text{NH}_2 \end{array} \begin{bmatrix} :\text{O:} & :\text{O:} & :\text{O:} \\ \end{bmatrix}^{4-} \\ \text{CH}_2 - \text{C$$

polydentate

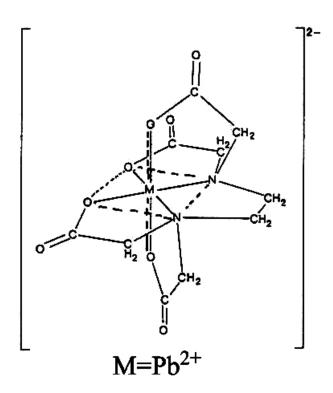


atoms forming coordinate covalent bonds indicated in **BLUE**

EDTA a chelate (claw!!)



hexadentate



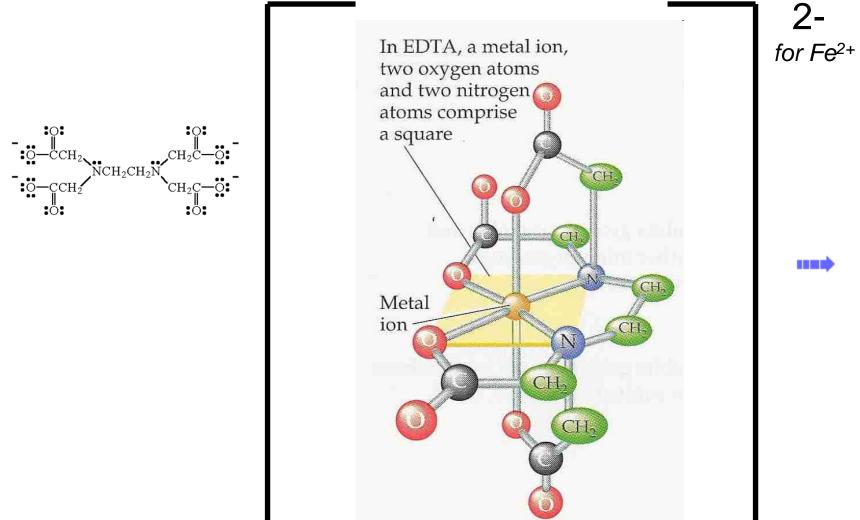


Table 19.13 , Figure 19.7

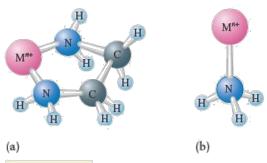
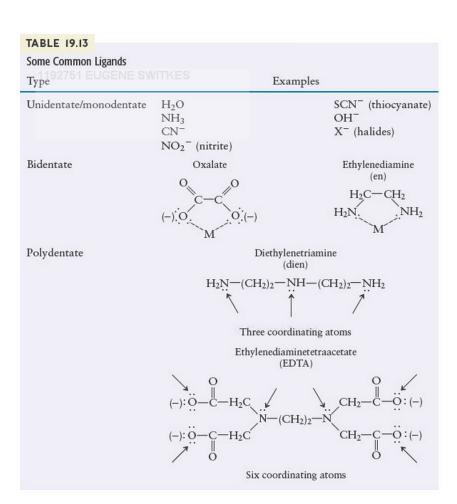


FIGURE 19.7

(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.



given $[Co(NH_3)_n]$ 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

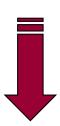


other examples

 $K_3[Fe(CN)_n]$ octahedral

[Co(en)_n]Cl₃ octahedral

Na₂[Ni(CN)_n] square planar



- General factoids about transition metals
- Nomenclature
- Isomerism



A bicycle with a titanium frame.



Manganese nodules on the sea floor.



hybridization involving d-orbitals:

d²sp³ six octahedrally oriented hybrids dsp³ four square planar hybrids

Crystal Field Theory of Coordination Complexes

magnetic properties and pretty colors

(PP 964-970)

have covered worksheet 10 I-III

Chemistry 18-AL Fall 2016, Study Guide and Worksheet X

Chemistry 18-AL Fall 2016, Study Guide and Worksheet X

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

Then ext 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

L.	A coordination complex is composed or a central atom or ion (offen 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
	ligand the	- -		
2.	In the coordination comple	([Cu(CN) ₄] ³⁻ the centra	alatom/ionis Cu	,the
	ligands are (CN)	, and the coordina	ation number is	1

II. Common Ligands

- In order to form a coordinate covalent bond the ligand must generally have one or more non-bonding pairs of electrons
- Why is ethylene diamine H₂NCH₂CH₂NH₂ 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.

omina, oxidations lates, d-electrona in cooldination compounds				
To calculate the number of ligands in a coordination complex you must				
i. know the coordination number of the complex from thegeometry				
of the complex ion, (or perhaps vice versa)				
ii. and the number of coordinate covalent bonds, the 'dentateness' of each ligance				
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.				
ocalculate the oxidation state of the metal ion you must				
i. know the <u>total charge</u> of the complex ion ii. and the <u>charge on each ligand</u> (multiplied by the number of				
ii. and the <u>Charge of each right o</u> (multiplied by the number of ligands)				
iganus) I. To calculate the number of d-electrons on the metal ions one applies the oxidation state or				
the metal and the Aufbau principle for positive ions.				
The transfer of particle and the transfer of				
. A tetra hedral complex of [CuCl.] ²⁻ has a total charge of 2-				
i. The number of chloride ligands, x, is				
ii. The oxidation state of the Cu ² ion is 2+				
iii. The number of d-electrons on the Cu^7 ion is $\underline{}^9$.				
Further links to the orientation of d-orbitals relative to coordination sites:				
Octahedral:				
http://switkes.chemistrv.ucsc.edu/teachine/CHEM1.B/Jmp1/CrvstalField/CFT_OrbsOctahedra				
Several geometries: http://www.them.uwimora.edu.jm1104/courses/CFT_Orbs.html				
Hemoglobin:				
http://switkes.chemistry.ucsc.edu/teaching/CHEMILB/WWW other links/ox deox hemo.ht				
Vagnetic and chromatic properties of transition metal complexes				

IV. Magnetic and chromatic properties of transition metal complex see: https://www.youtube.com/watch?y=xNXFSE7pxXM



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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



Chemistry 18-32 fell 2018, World Guide and Worldheet X

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HV#6 55, 57, 58, 59, 517, 518

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- 3. In operation of lower locks, a view who where we what we expend of a box of each engrishment allows who considers a box of a box of the light $\frac{|\nabla g|^{\frac{1}{2}}\nabla g|}{|\nabla g|^{\frac{1}{2}}\nabla g|}$.
- A moral for MT can form tox chood mathematical [MC40] \$\frac{1}{2}\tau^2 \text{ and [M1, \begin{align*} \text{ in the about would be light. Which come box is more body considers of \$\frac{1}{2}\text{ [M1, \begin{align*} \text{ in the about the

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IV. Magnetic and chromatic properties of transition metal complexes

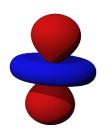
see: https://www.youtube.com/watch?v=xNXRSE7pxXM



crystal-field theory of transition metal coordination complexes

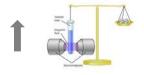


"reality" of the shapes of dorbitals

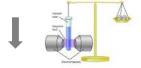




why are 'free' transition metal ions colorless?
 but
 transition metal ions in coordination complexes are often colored?



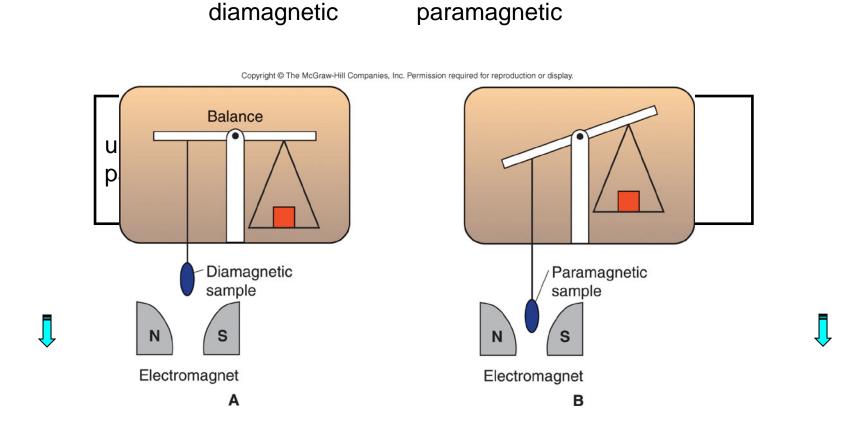




and others are paramagnetic?

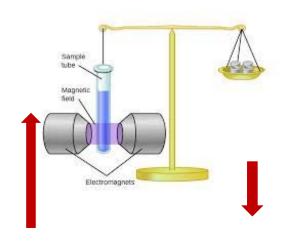
paramagnetism vs diamagnetism (Gouy balance)





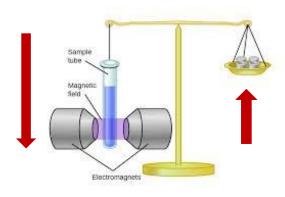
strength of paramagnetism depends on number of unpaired electrons

crystal field theory and magnetic properties [Co(NH₃)₆]³⁺ vs [Co(F)₆]³⁻



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

but



[Co(F)₆]³⁻ is paramagnetic

- most electronic excitations in UV (H 1s → H 2p λ=121 nm)
- Co^{3+} [Ar]3d⁶ \rightarrow Co^{3+} [Ar]3d⁵4s¹ (λ =75.3 nm) **UV** NH₃ \rightarrow NH₃* (excited state) (λ =216 nm) **UV**

Co³⁺ and NH₃ are colorless !!!

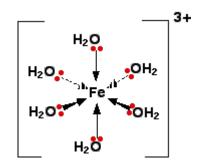
but in coordination complex

• $[Co(NH_3)_6]^{3+} \rightarrow excited state^* (\lambda=430 nm, absorbs 'indigo')$

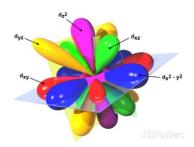


[NH₃)₆]³⁺ appears yellow-orange !!

 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.

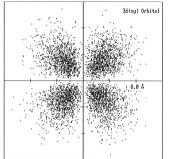


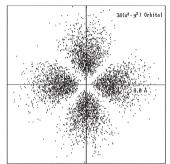


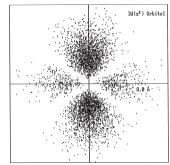
 Crystal field theory- an electrostatic approach to ligand-metal d-orbital interactions (more complicated ligand-field and m.o. approaches lead to similar predictions)

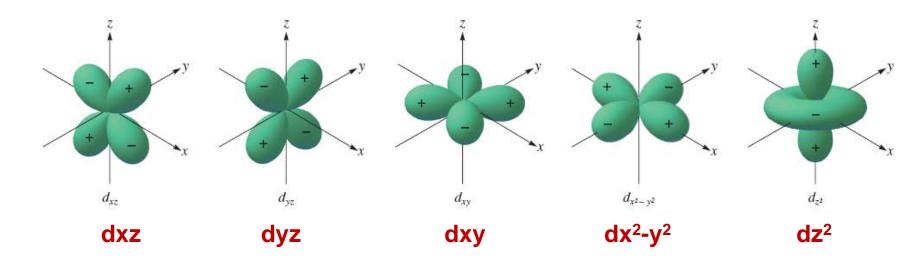
 Only responsible for octahedral complexes (other geometries follow similar considerations)

remember atomic d-orbitals (figure 12.21)

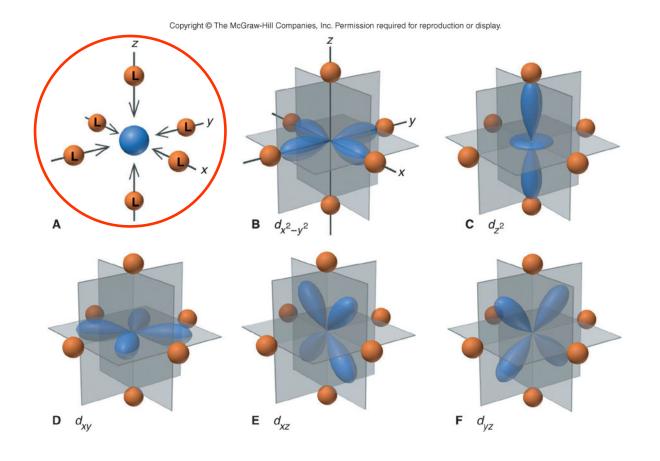


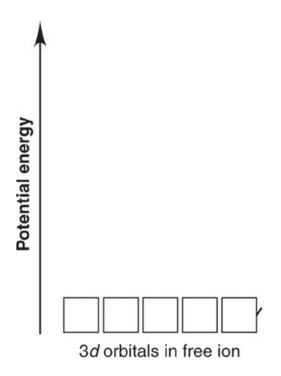






metal ion d-obitals in octahedral complex (Silberberg fig. 23.17; Zumdahl fig. 19.21)

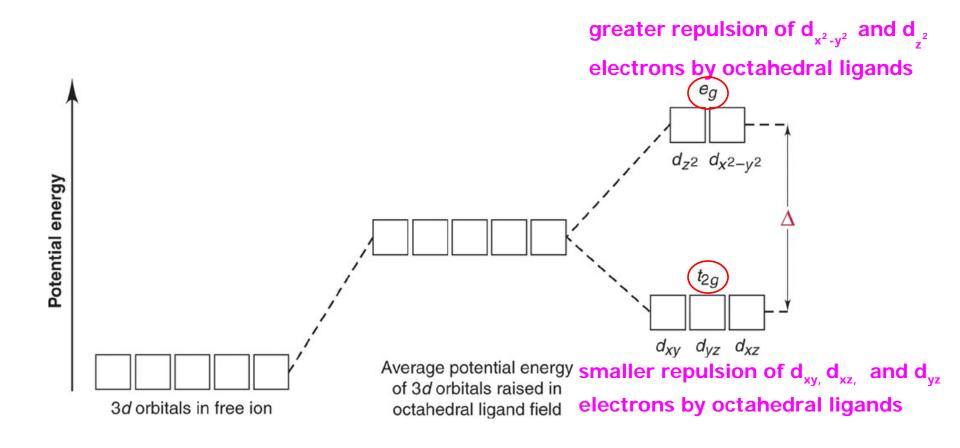




average ligand repulsion for metal d-electrons

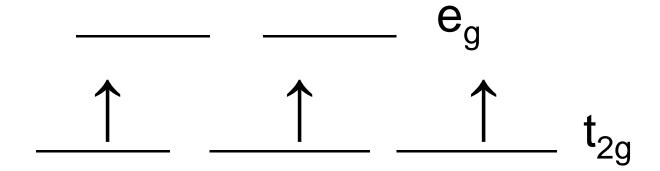
would each d-electron be repelled the same?





average ligand repulsion for metal d-electrons

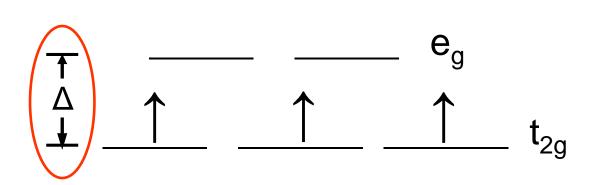
would each d-electron be repelled the same?



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

where does electron 4th go?

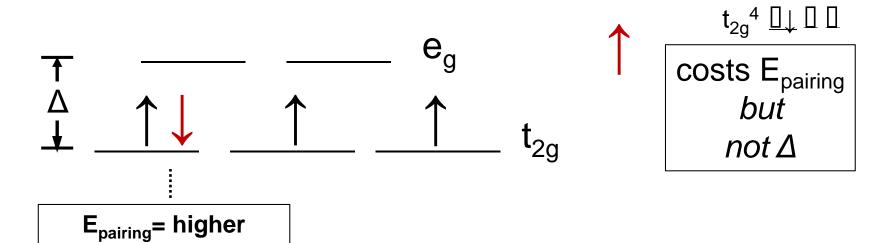
Δ vs ($E_{pairing}$): two possibilities for d^4

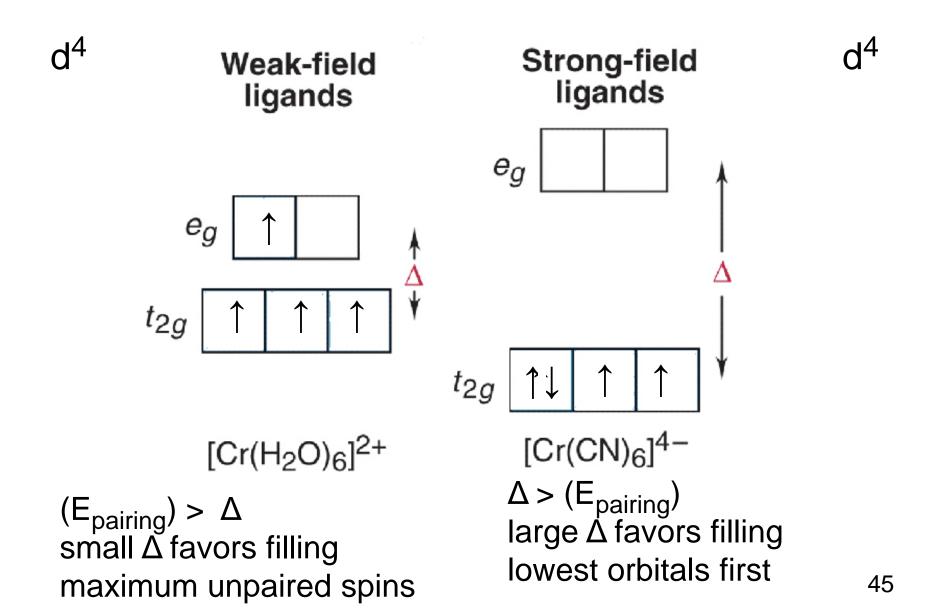


energy for paired vs

unpaired electrons

t_{2g}³ e_g
costs Δ (in energy)
but e's
remain unpaired



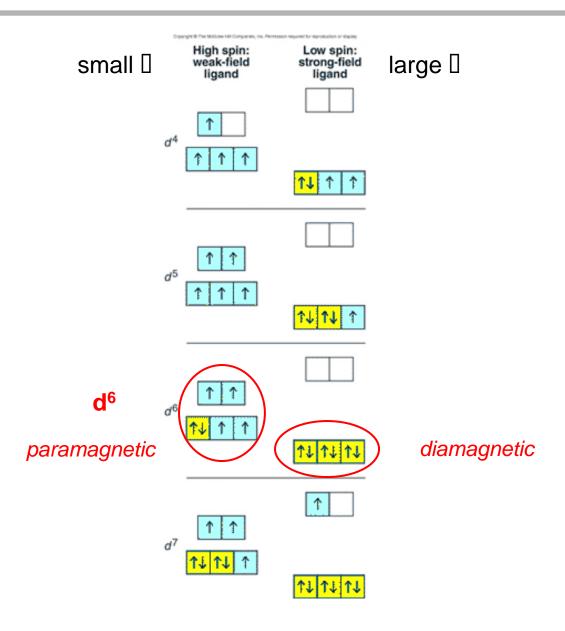


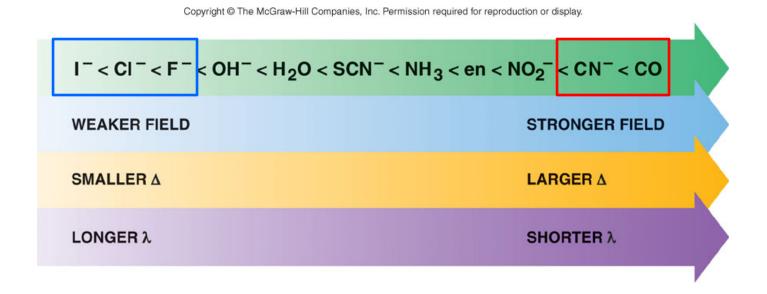
$[Cr(H_2O)_6]^{2+}$ VS $[Cr(CN)_6]^{4-}$

• $[Cr(H_2O)_6]^{2+}$, d^4 , weak-field \equiv high spin, $\frac{\uparrow}{\uparrow}$ $\frac{1}{2g}$ $t_{2g}^3e_g^1$ 4 unpaired electrons, paramagnetic

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

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

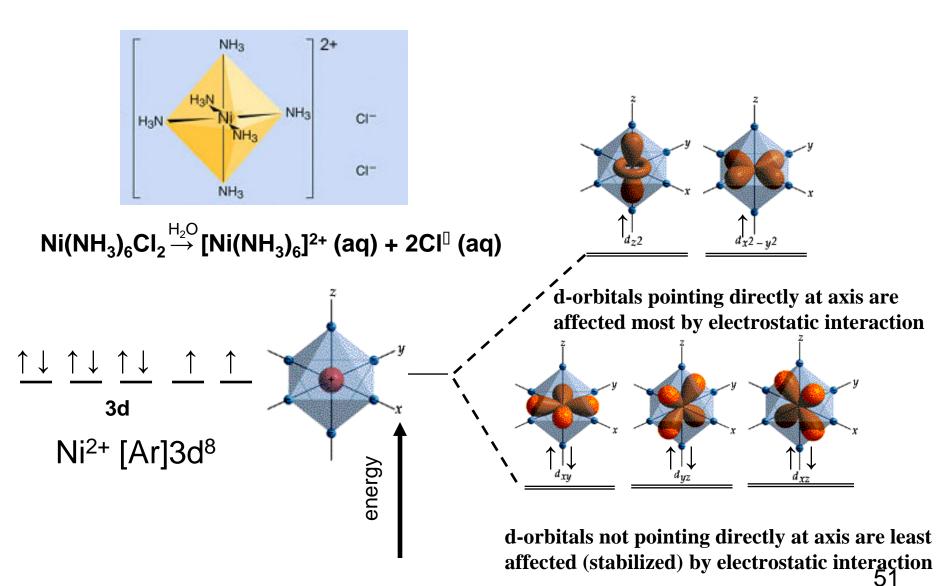




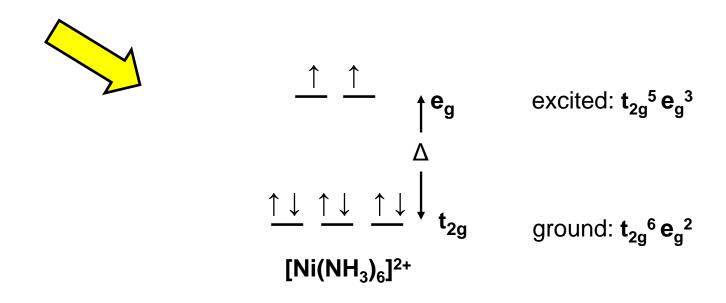
know: CN⁻, CO strong (high) field F -,Cl⁻, l⁻ (halogen anions) weak (low) field if using others you would be told which How are the magnetic properties of transition metal complexes related to the shape of d-orbitals?

 Why are transition metal complexes colored? 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.

d-Orbitals and ligand Interaction (octahedral field)



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

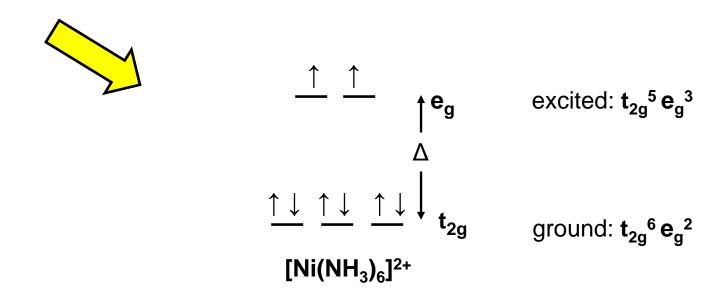


- larger Δ's correspond to absorbing shorter wavelengths
- how does the wavelength absorbed relate to the color perceived for various transition metal complex ions?
 [next class !!]



Perception of the Color of Objects

an addendum to Crystal Field Theory

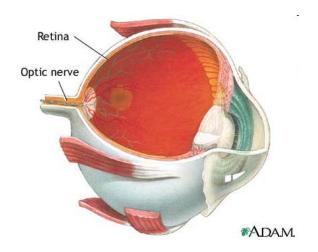


- larger Δ's correspond to absorbing shorter wavelengths
- how does the wavelength absorbed relate to the color perceived for various transition metal complex ions?

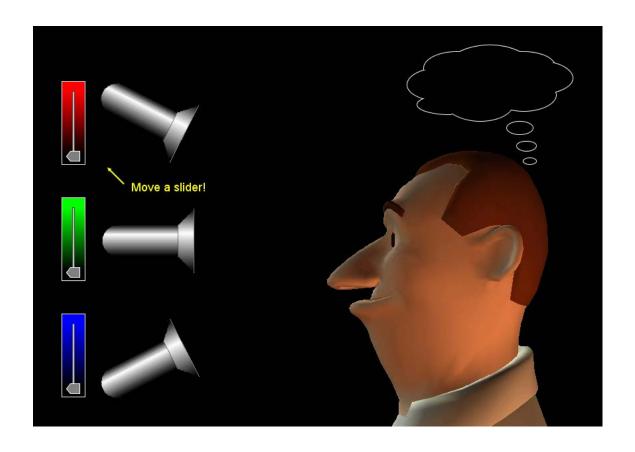
human vision and chemistry LATER in spectroscopy



• 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



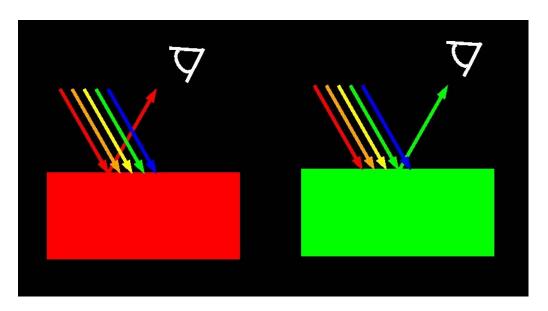
http://phet.colorado.edu/sims/color-vision/color-vision_en.jnlp





 The color of an object arises from the wavelengths reflected by the object and entering the eye

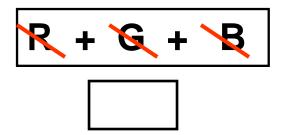
 If the object is viewed in white light (as is usual) the color seen is the complement of the wavelengths absorbed



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 (vellow-green) Violet Dark blue 580 (yellow) 600 (orange) Blue 650 (red) Green

reflects



```
(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 🛚
                 White
                  Yellow (R+G)
       В
       Cyan (G+B) Red
        G
       Y (R+G)
                 Blue
                  Black
        R+G+B
```

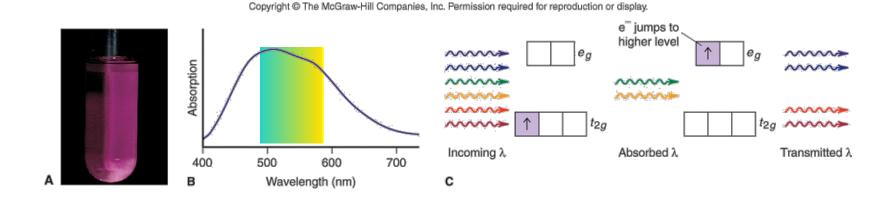
additive color mixing demo



subtractive color mixing demo



$$[Ti(H_2O)_6]^{3+}$$
 d¹



absorbs green-yellow appears purple



Hold your hands up and twist them, like you're brushing everything away.

All done or finished. Let's see you sign it!



colored transition metal complexes- glazes



 $Ni(NH_3)_6Br_2$

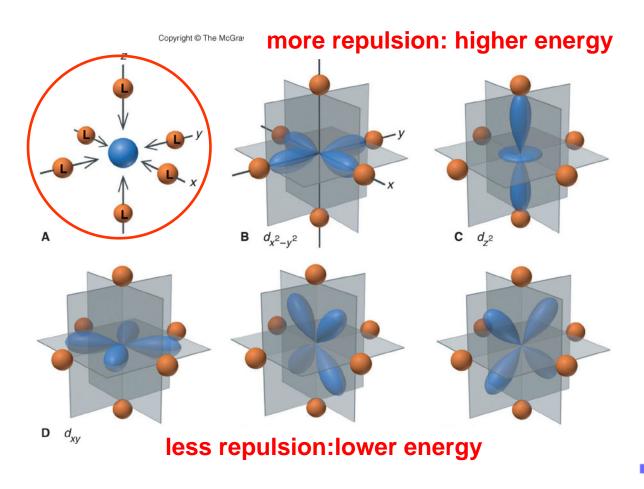


CoCl₂-6H₂O



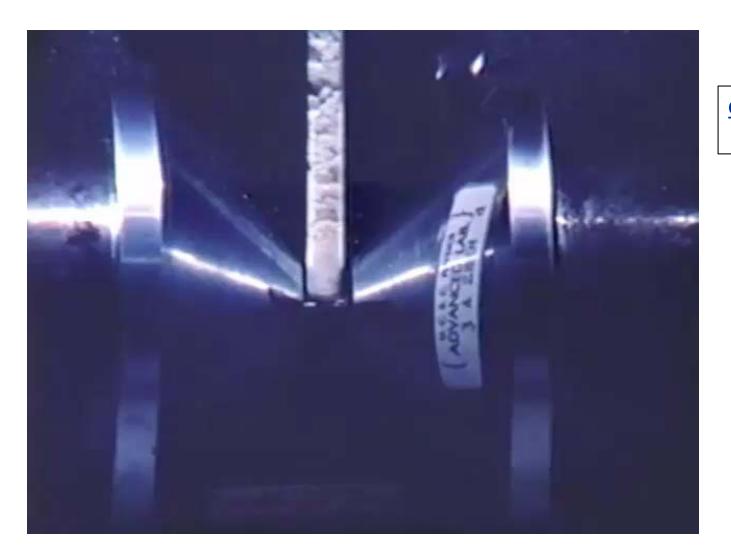
NiSO₄-6H₂O





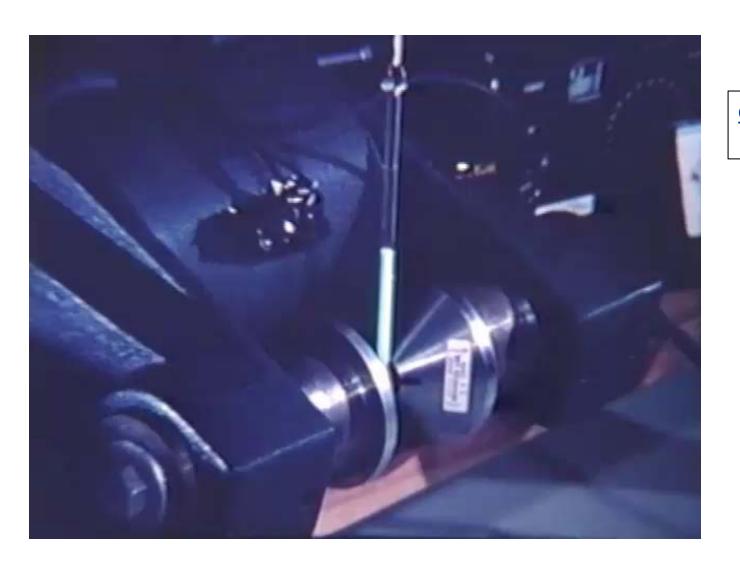
http://switkes.chemistry.ucsc.edu/teaching/CHEM1B/Jmol/CrystalField/CFT_OrbsOctahedral_java.html(java)





open video in browser



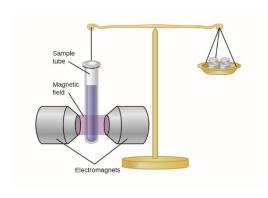


open video in browser



the Gouy (not the gooey !!) Balance





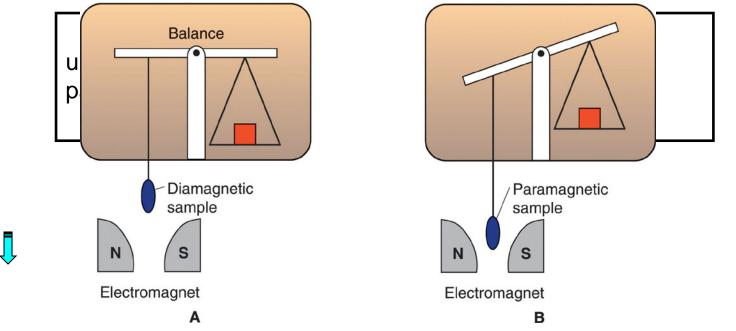


Louis Georges Gouy (1854-1926)





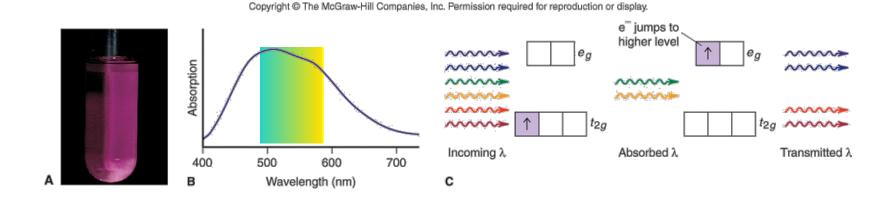
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strength of paramagnetism depends on number of unpaired electrons

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.

$$[Ti(H_2O)_6]^{3+}$$
 d¹



absorbs green-yellow appears purple

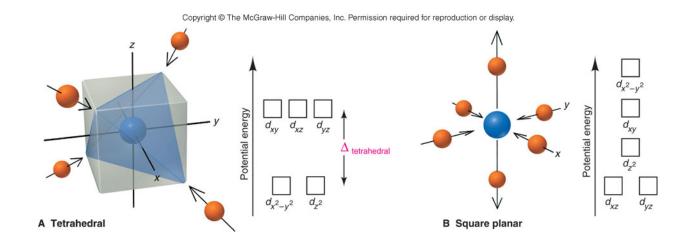
SO

$$\lambda = 124 \times 10^{-9} \,\mathrm{m}$$
 colorless

 $\lambda \approx 510 \times 10^{-9} \,\mathrm{m}$

appears purple

$$f = \frac{1}{2}$$
 3 [Ti(H₂O)₆]³⁺ d¹

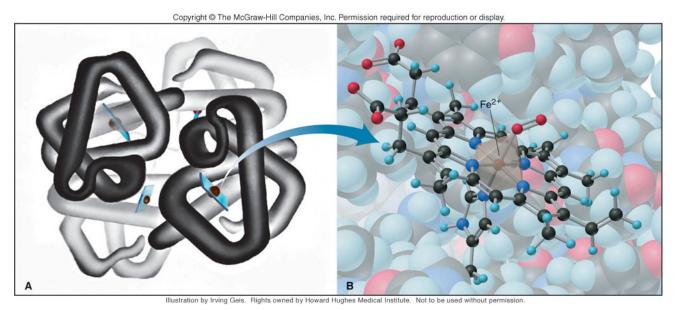


will not be on exams

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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 ₂ O 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

transition metal complexes in biology



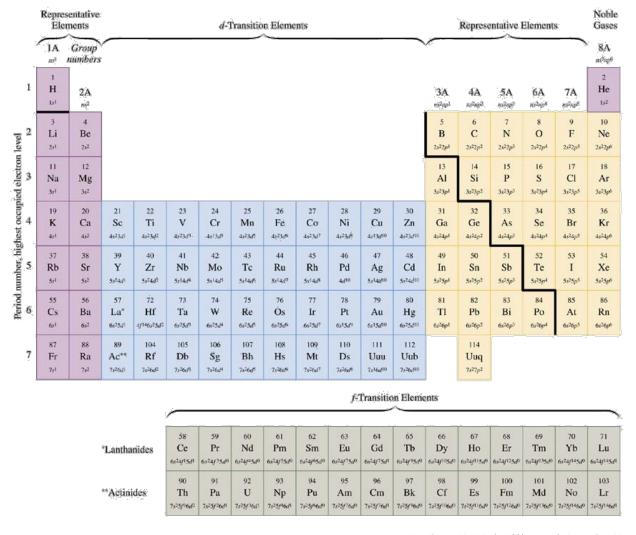
oxyheme

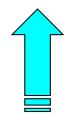
deoxyheme



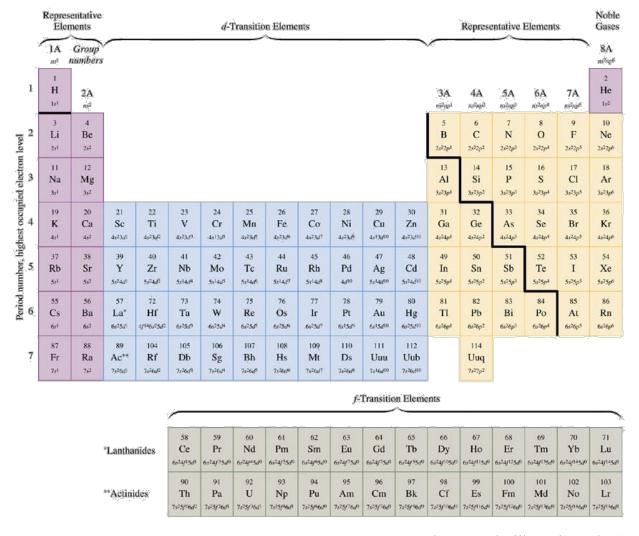
END

Zumdahl figure 12.29





Zumdahl figure 12.29





colored transition metal complexes- glazes





 $Ni(NH_3)_6Br_2$

CoCl₂-6H₂O

NiSO₄-6H₂O

