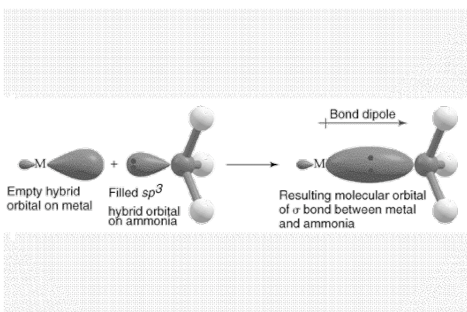
Coordination Chemistry

Crystal Field Theory

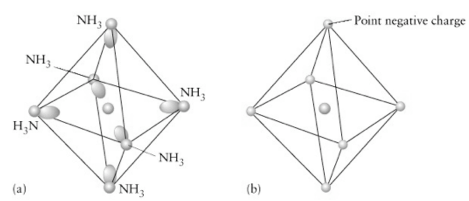
Crystal-Field Theory

- Crystal field theory describes bonding in transition metal complexes.
- The formation of a complex is a Lewis acid-base reaction.
- Both electrons in the bond come from the ligand and are donated into an empty, hybridized orbital on the metal.
- Charge is donated from the ligand to the metal.
- Assumption in crystal field theory: the interaction between ligand and metal is electrostatic.
- ***There are differences in the electrostatic interactions depending on the ligand. (Energy Differences)***

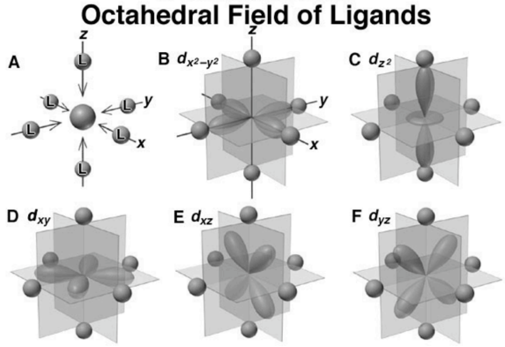
Crystal-Field Theory



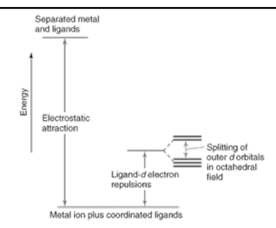
In the crystal field theory of complexes, the lone pairs of electrons (the Lewis base sites) on the ligands (a) are treated as equivalent to point negative charges (b).



d Orbitals in an Octahedral Field of Ligands

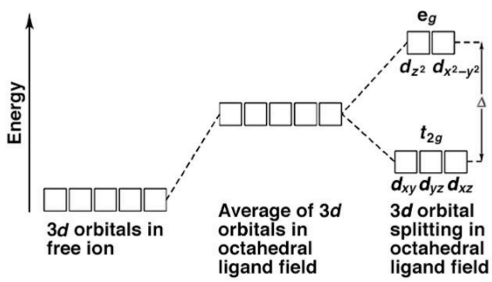


Crystal-Field Theory

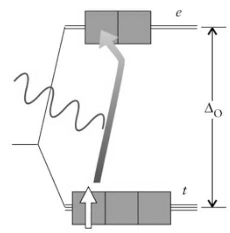


- The complex metal ion has a lower energy than the separated metal and ligands.
- In an octahedral field, the five *d* orbitals **do not** have the same energy: **Two** orbitals are **higher energy** than the other three orbitals.
- The energy gap between them is called Δ, the crystal field splitting energy.

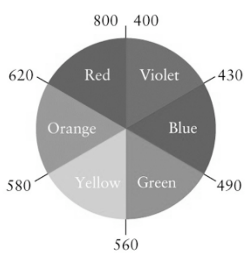
Splitting of *d*-Orbital Energies by an Octahedral Field of Ligands

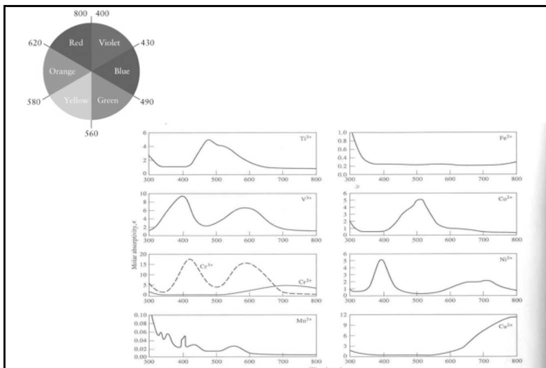


When a complex is exposed to light of the correct frequency, an electron can be excited to a higher energy orbital (from *t* to *e* if the complex is octahedral), and the light is absorbed.



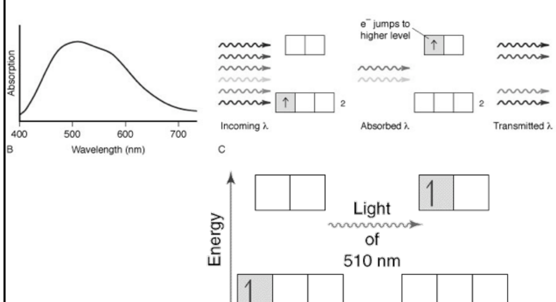
The perceived color of a complex in white light is the complementary color of the light it absorbs. In this color wheel, complementary colors are opposite each other. The numbers are approximate wavelengths in nanometers.





http://www.wou.edu/las/physci/ch462/tmcolors.htm

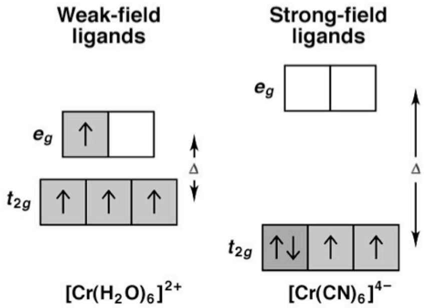
The Color of $[Ti(H_2O)_6]^{3+}$



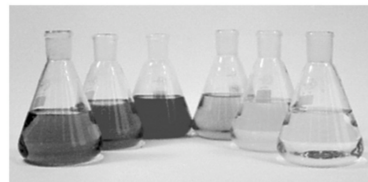
Crystal-Field Theory

- The energy gap is the crystal field splitting energy Δ.
- Ti^{3+} is a d^1 metal ion.
- For Ti^{3+}, the gap between energy levels, Δ is of the order of the wavelength of visible light.
- As the $[Ti(H_2O)_6]^{3+}$ complex absorbs visible light, the electron is promoted to a higher energy level.
- Since there is only one *d* electron there is only one possible absorption line for this molecule.
- Color of a complex depends on the magnitude of Δ which, in turn, depends on the metal and the types of ligands.

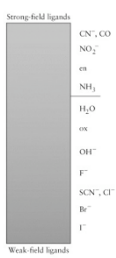
Effect of the Ligand on Splitting Energy

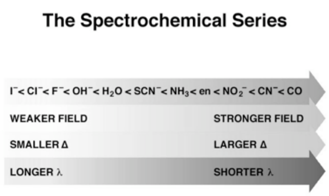


The effect of changing the ligands in octahedral cobalt(III) complexes in aqueous solution changes absorption and color. The ligand field strengths increase from left to right.



The spectrochemical series. Strong-field ligands give rise to a large splitting between the *t*- and *e*-orbitals, whereas weak-field ligands give rise to only a small splitting. The horizontal line marks the frontier between the two kinds of ligands. The change in color of the bar represents the increasing energy of light absorbed as the field strength increases.





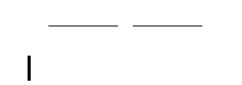
Electronic Configurations of Transition Metal Complexes

d orbital occupancy depends on Δ (ligand(s)) and pairing energy, P

- e^-'s assume the electron configuration with the lowest possible energy cost
- If Δ > P (Δ large; strong field ligand)
  - e^-'s pair up in lower energy d subshell first
- If Δ < P (Δ small; weak field ligand)
  - e^-'s spread out among all d orbitals before any pair up

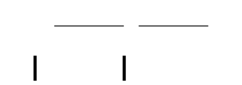
d-orbital energy level diagrams octahedral complex

d^1



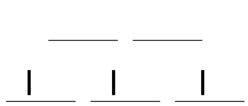
d-orbital energy level diagrams octahedral complex

d^2



d-orbital energy level diagrams
octahedral complex

d^3



d-orbital energy level diagrams
octahedral complex

d^4

high spin
$\Delta < P$

low spin
$\Delta > P$

d-orbital energy level diagrams
octahedral complex

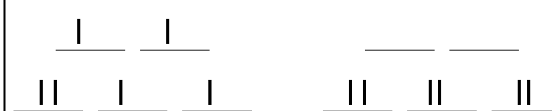
d^5

high spin
$\Delta < P$

low spin
$\Delta > P$

d-orbital energy level diagrams
octahedral complex

d^6



high spin
$\Delta < P$

low spin
$\Delta > P$

d-orbital energy level diagrams
octahedral complex

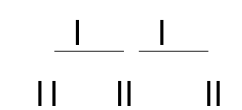
d^7

high spin
$\Delta < P$

low spin
$\Delta > P$

d-orbital energy level diagrams
octahedral complex

d^8



d-orbital energy level diagrams octahedral complex

d^9

__||__ __|__

__||__ __||__ __||__

d-orbital energy level diagrams octahedral complex

d^{10}

__||__ __||__

__||__ __||__ __||__

QUESTION

The complex ions of Zn^{2+} are all colorless. The most likely explanation for this is:

A) Zn^{2+} is paramagnetic.
B) Zn^{2+} exhibits *d*-orbital splitting in its complexes such that all wavelengths in the visible region are absorbed.
C) Since Zn^{2+} is a d^{10} ion, it does not absorb visible light even though the *d*-orbital splitting is correct for absorbing visible wavelengths.
D) Zn^{2+} is not a transition metal ion.
E) None of these are correct.

Electronic Configurations of Transition Metal Complexes

- Determining d-orbital energy level diagrams:
  - determine oxidation # of the metal
  - determine # of d e^-'s
  - determine if ligand is weak field or strong field
  - draw energy level diagram

Spectrochemical Series

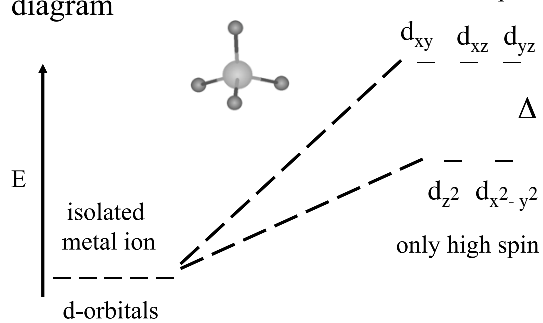
Smallest Δ → Δ increases → Largest Δ

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < CN^-$

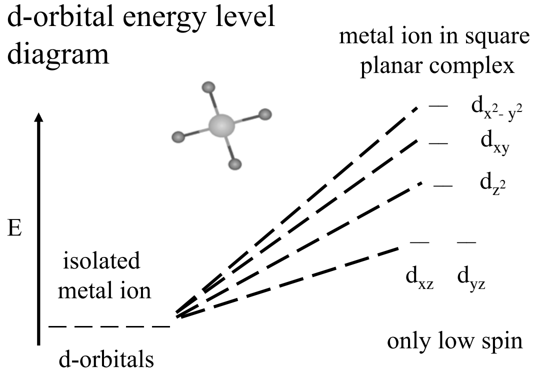
weak field   strong field

d-orbital energy level diagram

metal ion in tetrahedral complex



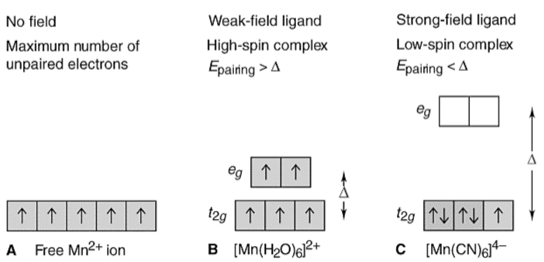
d-orbital energy level diagram



Magnetism

- Paramagnetic metal complexes have unpaired electrons.
- Diamagnetic metal complexes have paired electrons.
- There are some interesting observations. Consider a d^6 metal ion:
  - $[Co(NH_3)_6]^{3+}$ has no unpaired electrons, but $[CoF_6]^{3-}$ has four unpaired electrons per ion.
- Strong Field (low spin) vs. Weak Field (high spin) provide an explanation.

High-spin and low-spin complex ions of Mn^{2+}

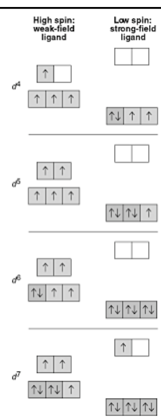


QUESTION

Which of the following is paramagnetic?

A) $Zn(H_2O)_6^{2+}$
B) $Co(NH_3)_6^{3+}$ (strong field)
C) $Cu(CN)_3^{2-}$
D) $Mn(CN)_6^{2-}$ (strong field)
E) None of these

Orbital Occupancy for High- and Low-Spin Complexes of d^4 Through d^7 Metal Ions

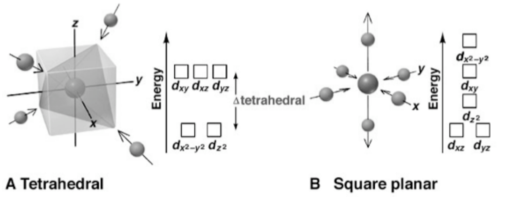


QUESTION

How many unpaired electrons are found in the octahedral complex ion $[CoI_6]^{3-}$? Note: I^- is considered to be a weak field ligand.

1. one
2. two
3. three
4. four

Splitting of *d*-orbital Energies by a Tetrahedral Field and a Square Planar



High spin **Low spin**

QUESTION

The geometry of a coordination compound with a coordination number of 4 is

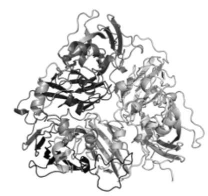
A. tetrahedral, in order to minimize repulsions between the ligands
B. octahedral, since there are two different positions possible for each ligand
C. square planar, to allow room for the counterion because the ligands take up so much space
D. linear, since there are two ligands on each side of the transition metal
E. tetrahedral or square planar, but too difficult to predict based on the information given

Some Transition Metal Trace Elements in Humans

Element	Biomolecule Containing Element	Function of Biomolecule
Chromium	Glucose tolerance factor	Glucose utilization
Manganese	Isocitrate dehydrogenase	Cell respiration
Iron	Hemoglobin and myoglobin	Oxygen transport
	Cytochrome *c*,	Cell respiration; ATP form.
	Catalase	Decomposition of H_2O_2
Cobalt	Cobalamin (vitamin B_{12})	Development of red blood cells
Copper	Ceruloplasmin	Hemoglobin synthesis
[*AA lab*]	Cytochrome oxidase	Cell respiration; ATP syn.
Zinc		
	Carboxypeptidase A	Protein digestion
	Alcohol dehydrogenase	Metabolism of ethanol
	Carbonic anhydrase	Elimination of CO_2

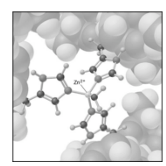
http://www.rcsb.org/pdb/101/motm.do?momID=49

Ceruloplasmin



Main Copper Transport Enzyme
&
Hemoglobin Catalyst

Carbonic Anhydrase

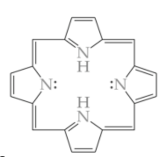


Tetrahedral Zn^{2+} Complex

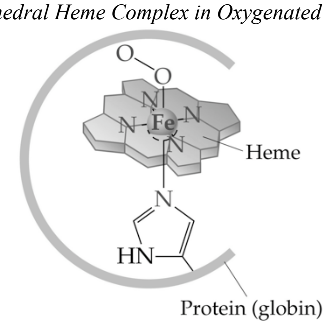
http://www.rcsb.org/pdb/explore/jmol.do?structureId=1KCW&bionumber=1

Living System Chelates

- Many natural chelates include a porphyrin molecule.
- A porphyrin is a tetradentate ligand.
- Porphyrins have been explored in Photodynamic Therapies (PDT)
- Two important metalloporphyrin complexes are heme (Fe^{2+}) and chlorophyll (Mg^{2+}).



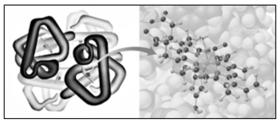
Octahedral Heme Complex in Oxygenated Blood

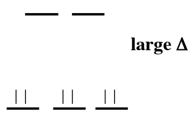


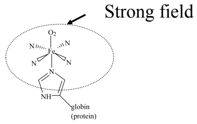
http://www.chemcollective.org/applets/everest/everest.php

Arterial Blood:

Octahedral Heme Complex



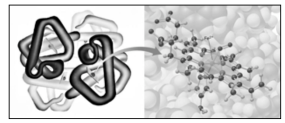


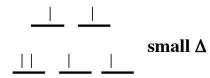


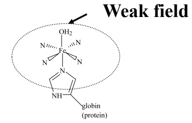
Bright red due to absorption of green

Venous Blood:

Octahedral Heme Complex







Bluish color due to absorption of orange

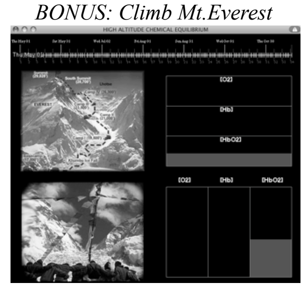
QUESTION

When water occupies one of the six sites around Fe^{2+} in hemoglobin (a weak field case), how many unpaired *d* electrons are found in the iron ion?

A. Four
B. One
C. Two
D. Three

Hemoglobin & Oxygenated Blood

BONUS: Climb Mt.Everest



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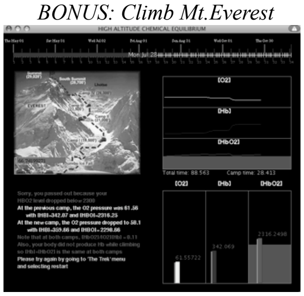
Hemoglobin & Oxygenated Blood

BONUS: Climb Mt.Everest



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Chlorophyll

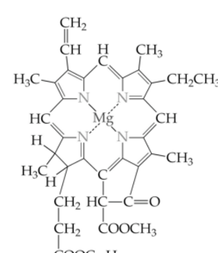
•Photosynthesis requires chlorophyll.

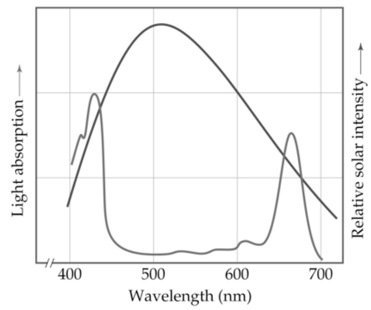
$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

The reaction capture energy from sunlight. It is highly endothermic.

•One mole of sugar requires 48 moles of photons.

•Chlorophyll absorbs red and blue light and is green in color.





Ligands with More than One Donor Atom

$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$

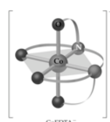
$K_f = 4 \times 10^8$

$[Ni(H_2O)_6]^{2+}(aq) + 3en \rightleftharpoons [Ni(en)_3]^{2+}(aq) + 6H_2O(l)$

$K_f = 2 \times 10^{18}$

- Sequestering agents are chelating agents that are used to remove unwanted metal ions.
- In medicine sequestering agents are used to selectively remove toxic metal ions: Hg^{2+} and Pb^{2+} in particular, while leaving biologically important metals.

Ligands with More than One Donor Atom



$CoEDTA^-$

- One very important chelating agent is ethylenediaminetetraacetate ($EDTA^{4-}$).
- EDTA has 6 coordination sites, for cobalt $[Co(EDTA)]^-$ is an octahedral Co^{3+} complex.
- Both N atoms (blue) and O atoms (red) coordinate to the metal.
- EDTA is used in consumer products to complex the metal ions which catalyze decomposition reactions.

Metal Toxicity and Chelation Treatments

NOTE: There is no chelation agent for Mn, nor Ni and Zn

Table. Typical Presentation of the Most Commonly Encountered Metals and Their Treatment

Metal	Acute	Chronic	Toxic Concentration	Treatment
Copper	Blue vomitus, GI irritation/ hemorrhage, hemolysis, MODS (ingested); MFF (inhaled)	vineyard sprayer's lung (inhaled); Wilson disease (hepatic and basal ganglia degeneration)	Normal excretion: 25 μg/24 h (urine)	BAL D-Penicillamine Succimer
Iron	Vomiting, GI hemorrhage, cardiac depression, metabolic acidosis	Hepatic cirrhosis	Nontoxic: < 300 μg/dL Severe: >500 μg/dL	Deferoxamine
Lead	Nausea, vomiting, encephalopathy (headache, seizures, ataxia, obtundation)	Encephalopathy, anemia, abdominal pain, nephropathy, foot-drop/ wrist-drop	Pediatric: symptoms or [Pb] ≥45 μ/dL (blood); Adult: symptoms or [Pb] ≥70 μ/dL[1]	BAL $CaNa_2$ EDTA Succimer
Manganese	MFF (inhaled)	Parkinson-like syndrome, respiratory, neuropsychiatric[2]	No clear reference standard	*
Mercury	Elemental (inhaled): fever, vomiting, diarrhea, ALI; Inorganic salts (ingestion): caustic gastroenteritis	Nausea, metallic taste, gingivo-stomatitis, tremor, neurasthenia, nephrotic syndrome; hypersensitivity (Pink disease)	Background exposure "normal" limits: 10 μg/L (whole blood); 20 μg/L (24-h urine)	BAL Succimer DMPS (Europe)