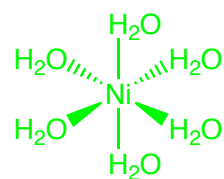


Chapter 19 Coordination Complexes

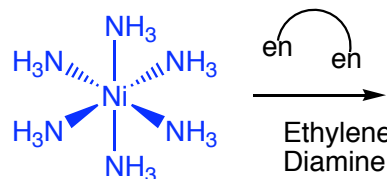
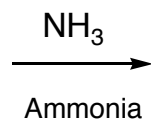
- 19.1 The Formation of Coordination Complexes
- 19.2 Structures of Coordination Complexes
- 19.3 Crystal-Field Theory and Magnetic Properties
- 19.4 The Colors of Coordination Complexes
- 19.5 Coordination Complexes in Biology

Infrared spectroscopy (IR tutor)

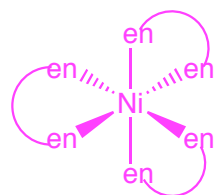
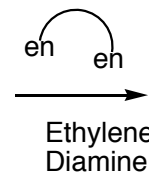
Ligand substitutions and color changes: Ni²⁺



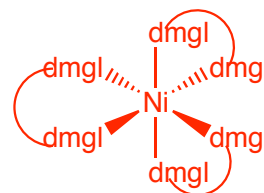
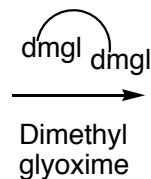
Green



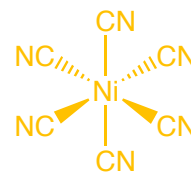
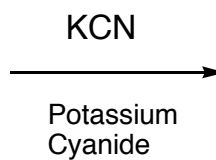
Blue



Purple



Pink



Yellow

OBITUARY

NOBELIST RICHARD SMALLEY DEAD AT 62

Codiscoverer of C_{60} , a new form of carbon, did much to advance science

RICHARD E. SMALLEY, A GIANT in the field of nanotechnology who shared in the 1996 Nobel Prize in Chemistry for the discovery of fullerenes, died on Oct. 28 after a seven-year battle with leukemia. He was 62.

Smalley spent most of his career at Rice University, where he was a professor of chemistry and of physics and founding director of the Center for Nanoscale Science & Technology.

He shared the Nobel Prize with fellow Rice chemist Robert F. Curl Jr. and British chemist Sir Harold W. Kroto for their 1985 discovery of buckminsterfullerene ("buckyball"), a new form of carbon. The finding of this 60-carbon cage molecule opened a new field of research that led to the discovery, elsewhere, of carbon nanotubes—tubular fullerenes that soon became the focus of Smalley's research. Over the years, he and his coworkers developed improved methods for making high-quality single-walled nanotubes, which are highly desired for many applications.

Smalley considered nanotubes to be a wondrous material that could help humanity achieve some of its most challenging goals, such as the quest for clean, inexpensive energy. In 2000, he helped found Carbon Nanotechnologies Inc. to produce "buckytubes" for the benefit of society.

Smalley also became a peripatetic spokesman for nanotechnology, crisscrossing the country to

give speeches, testify before Congress, and meet with government, academic, and industrial leaders. In 1999, he supported the National Nanotechnology Initiative and is credited with playing a crucial role in getting it approved by Congress. Federal spending for this sweeping R&D program is topping \$1 billion this year.

Even before his work with fullerenes, Smalley had made important contributions. He pioneered the use of supersonic jet cooling in conjunction with laser spectroscopy to simplify complex spectra and observe van der Waals molecules and free radicals. He also combined laser vaporization, jet cooling, and laser spectroscopy to study metal clusters and their chemistry. This work led to his study of carbon clusters and the discovery of fullerenes.

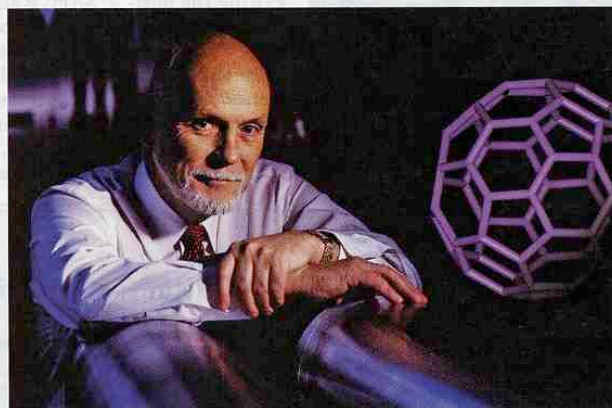
Any one of these accomplishments would make for "a rather good career for most scientists," Curl tells C&EN. "Taken together, they are simply breathtaking."

Smalley's scientific colleagues remember him for his intensity, focus, and passion for science. "His mind was like a searchlight bringing whatever it looked at into clarity," Curl says. "He was such a fighter that, until the last few days, I believed he would beat the can-

cer, just as he succeeded in beating all technical problems."

"He was always an iconoclast, always looking for the unexpected, the signal he didn't understand," remembers Naomi J. Halas, another Rice colleague. Projects that went as expected tended to bore him, she says.

One of Smalley's most ambitious programs was launched in April with \$11 million in funding from NASA. The program is aimed at the construction of a "quantum wire"—a continuous cable of carbon nanotubes that, Smalley said, "will conduct elec-



RICE UNIVERSITY PHOTO

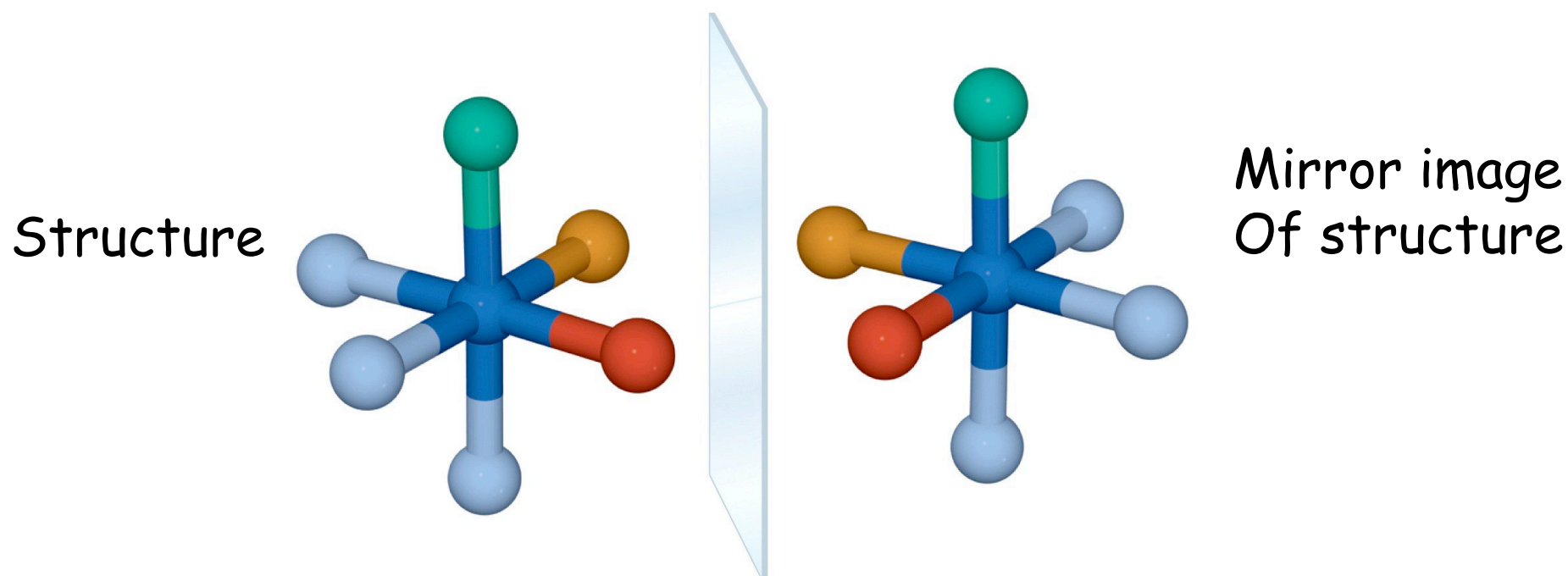
Richard E. Smalley
1943–2005

tricity 10 times better than copper yet have only one-sixth the weight ... and a tensile strength greater than steel. If we succeed, we'll be able to rewire the world, replacing aluminum and copper in virtually every application and permitting a vast increase in the capacity of the nation's electrical grid."

Rice chemistry professor James M. Tour, a close friend and collaborator, marvels at the intricately detailed drawings of equipment that Smalley included in his research notebook. "It reminded me of the notebooks of Leonardo da Vinci—the musings of a genius," Tour says. "Indeed, a Leonardo da Vinci has passed."—RON DAGANI

Enantiomers: non superimposable mirror images

A structure is termed *chiral* if it is not superimposable on its mirror image (we use idealized geometric structures with ligands considered as points)



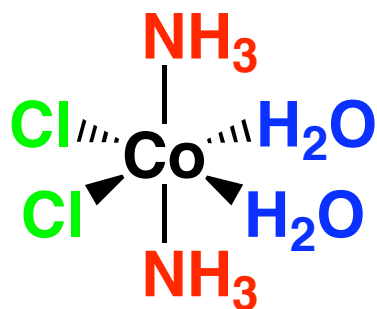
Two chiral structures: non superimposable mirror images

How do we decide if two structures are superimposable?₄

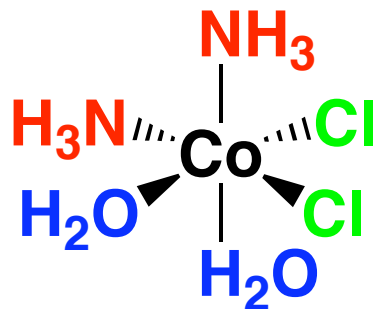
Chirality: the absence of a plane of symmetry:
Enantiomers are possible

A molecule possessing a plane of symmetry is **achiral** and
a superimposable on its mirror image
Enantiomers are NOT possible

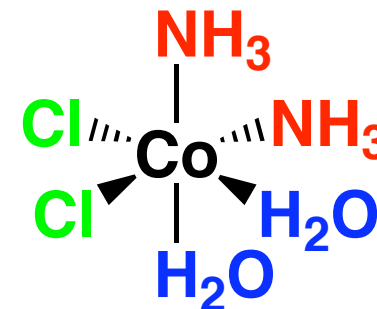
Are the following chiral or achiral structures?



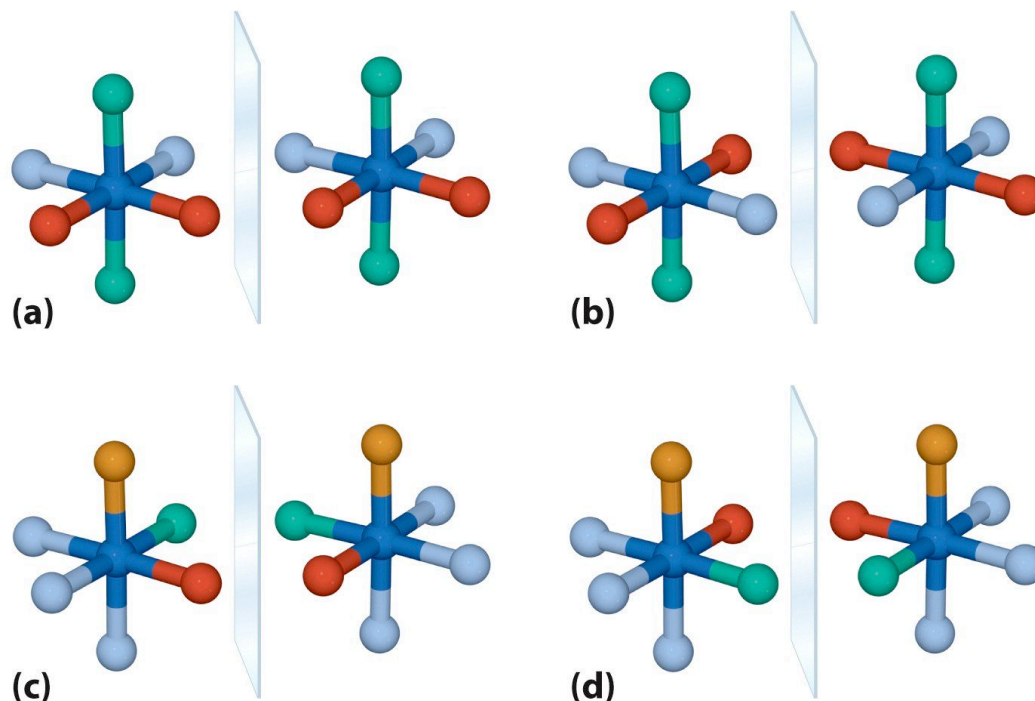
Plane of symmetry
Achiral (one structure)



No plane of symmetry
Chiral (two enantiomer)



Which are enantiomers (non-superimposable mirror images) and which are identical (superimposable mirror images)?



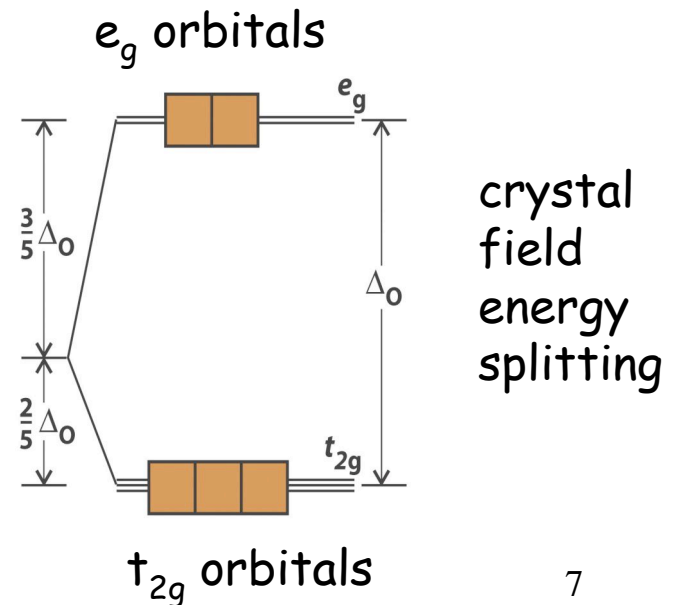
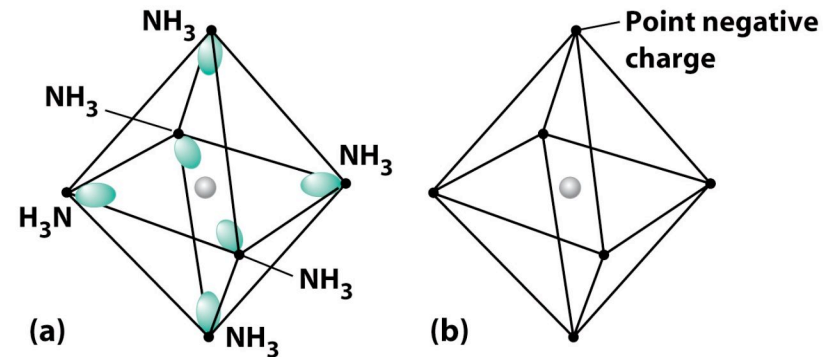
Look for a plane of symmetry in idealized geometric structures: If there is one the mirror images are the same structure. If there is not one, the mirror images are enantiomers (optical isomers).

19.3 Crystal Field Theory: Splitting of the 5 d orbitals

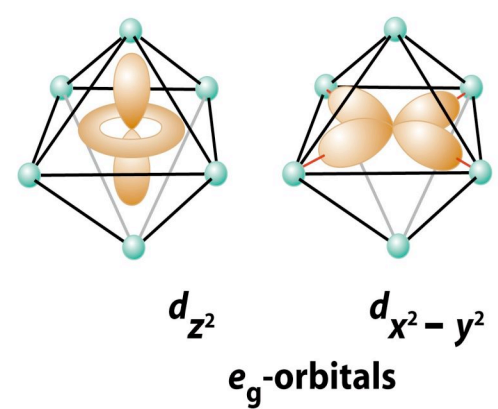
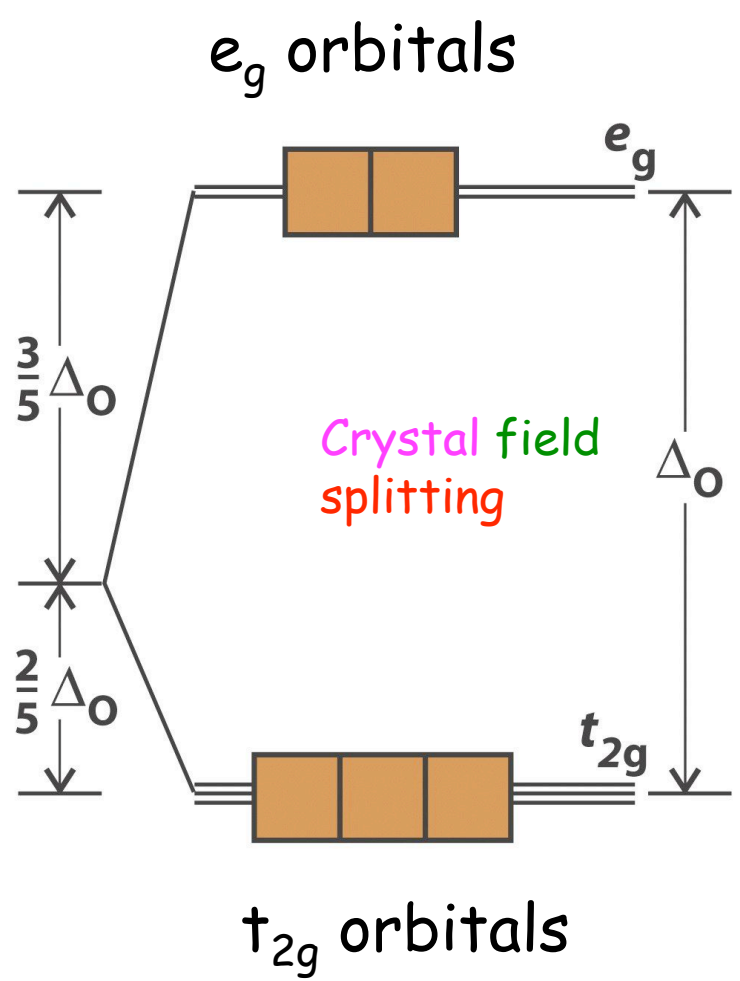
Consider the response of the energy of the d orbitals to the approach of 6 negatively charged ligands (a "crystal field") along the x, y and z axes of the metal

The two d orbitals ($d_{x^2-y^2}$ and d_{z^2}) that are directed along the x, y and z axes are affected more than the other three d orbitals (d_{xy} , d_{xz} and d_{yz})

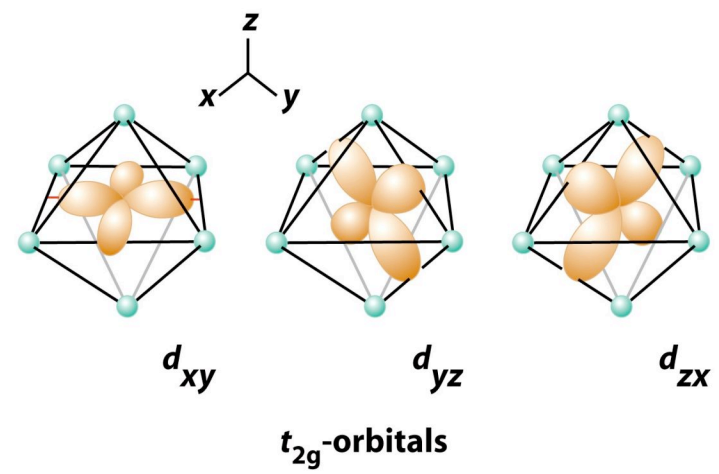
The result is that the $d_{x^2-y^2}$ and d_{z^2} orbital increase in energy relative to the d_{xy} , d_{xz} and d_{yz} orbitals (D_0 is called the "crystal field energy splitting")



Crystal field splitting of the 5 d orbitals by the "crystal field" of 6 ligands



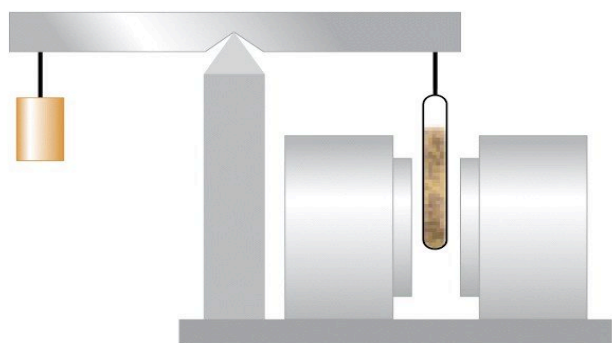
Orbitals "on axis": "energy increases"



Orbitals "off axis": "energy decreases"

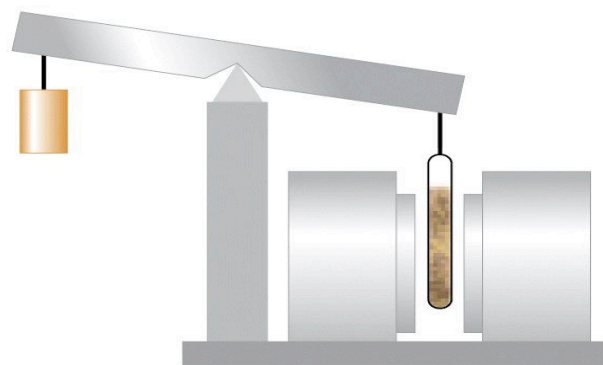
Electronic configurations of d^n complexes from paramagnetism and diamagnetism

Magnet off



(a)

Magnet on:
Paramagnetic



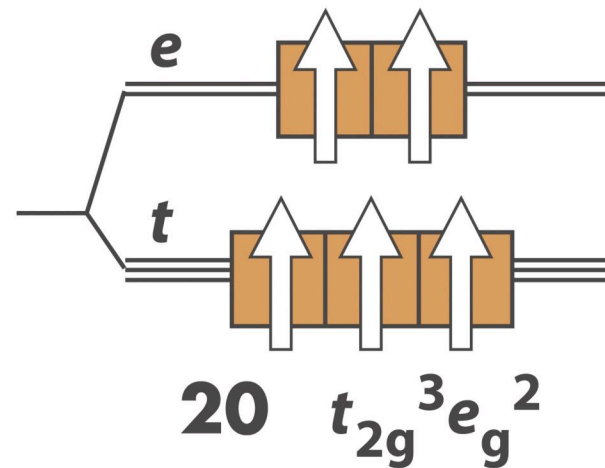
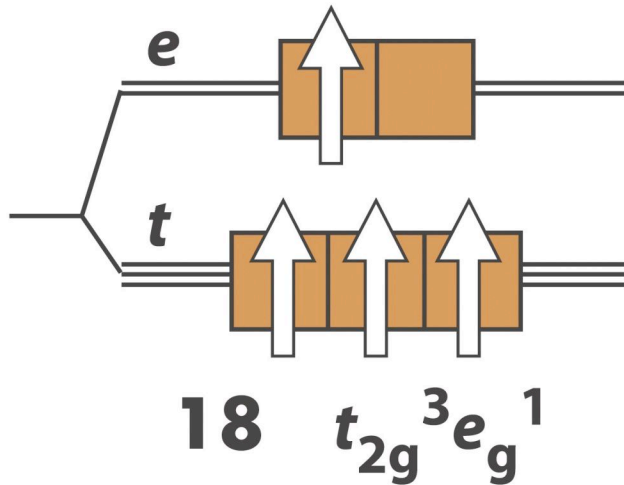
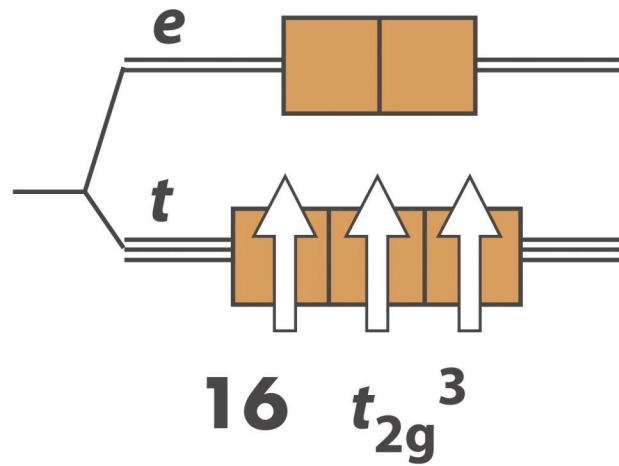
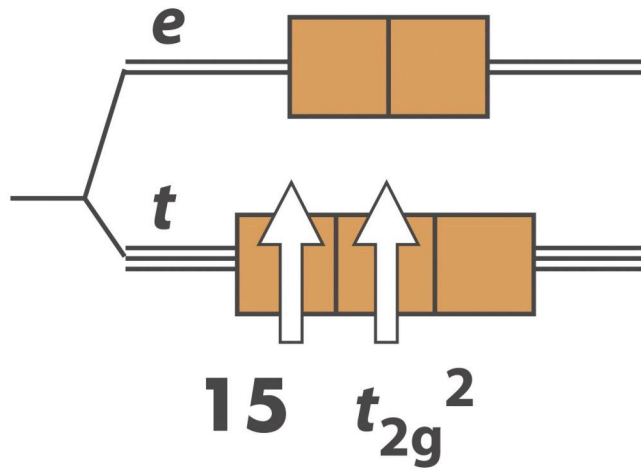
(b)



(c)

Magnet on:
diamagnetic

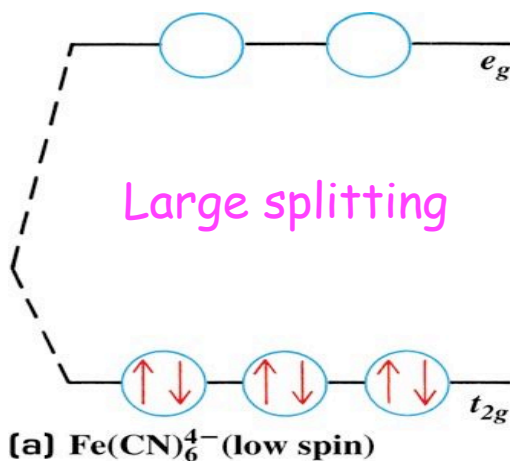
Building of weak field, high spin electron configurations for d^2 , d^3 , d^4 , and d^5 systems (Hund's rule applies)



Crystal Field Splitting of d orbitals: high spin and low spin situations for a d^6 metal

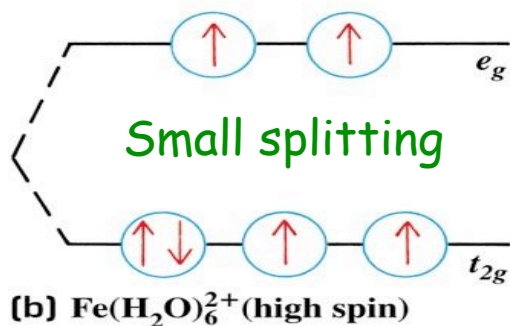
Ligand strength: (Weak) $I^- < F^- < H_2O < NH_3 < CN^-$ (Strong)

Low spin
Electrons spin pair



Net unpaired spins = 0:
Diamagnetic

High spin
Electrons do not spin pair



Net unpaired spins = 4:
Strongly paramagnetic

The d^n electron configurations of $M(\text{II})$ cations of the atoms of transition metals

Element	Neutral atom	2+ Ion	3+ Ion
Sc	$[\text{Ar}]4s^23d^1$	$[\text{Ar}]3d^1$	$[\text{Ar}]$
Ti	$[\text{Ar}]4s^23d^2$	$[\text{Ar}]3d^2$	$[\text{Ar}]3d^1$
V	$[\text{Ar}]4s^23d^3$	$[\text{Ar}]3d^3$	$[\text{Ar}]3d^2$
Cr	$[\text{Ar}]4s^13d^5$	$[\text{Ar}]3d^4$	$[\text{Ar}]3d^3$
Mn	$[\text{Ar}]4s^23d^5$	$[\text{Ar}]3d^5$	$[\text{Ar}]3d^4$
Fe	$[\text{Ar}]4s^23d^6$	$[\text{Ar}]3d^6$	$[\text{Ar}]3d^5$
Co	$[\text{Ar}]4s^23d^7$	$[\text{Ar}]3d^7$	$[\text{Ar}]3d^6$
Ni	$[\text{Ar}]4s^23d^8$	$[\text{Ar}]3d^8$	$[\text{Ar}]3d^7$
Cu	$[\text{Ar}]4s^13d^{10}$	$[\text{Ar}]3d^9$	$[\text{Ar}]3d^8$
Zn	$[\text{Ar}]4s^23d^{10}$	$[\text{Ar}]3d^{10}$	$[\text{Ar}]3d^9$

How many unpaired spins in $\text{Fe}(\text{CN})_6^{4-}$ and in $\text{Fe}(\text{H}_2\text{O})_6^{2+}$?

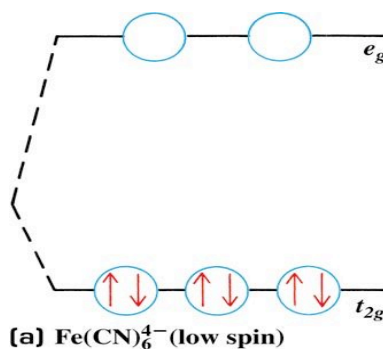
What is the charge of Fe in $\text{Fe}(\text{CN})_6^{4-}$ and in $\text{Fe}(\text{H}_2\text{O})_6^{2+}$?

Fe^{2+} in both cases $\text{Fe} = [\text{Ar}]3d^64s^2$; $\text{Fe}^{2+} = [\text{Ar}]3d^6$

What kind of ligands are CN^- and H_2O ?

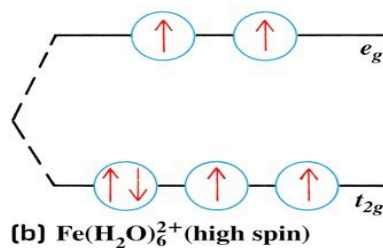
CN^- is a strong field ligand and H_2O is a weak field ligand

Large splitting
Low spin



Energy gap larger than advantage due to Hund's rule

Small splitting
High spin

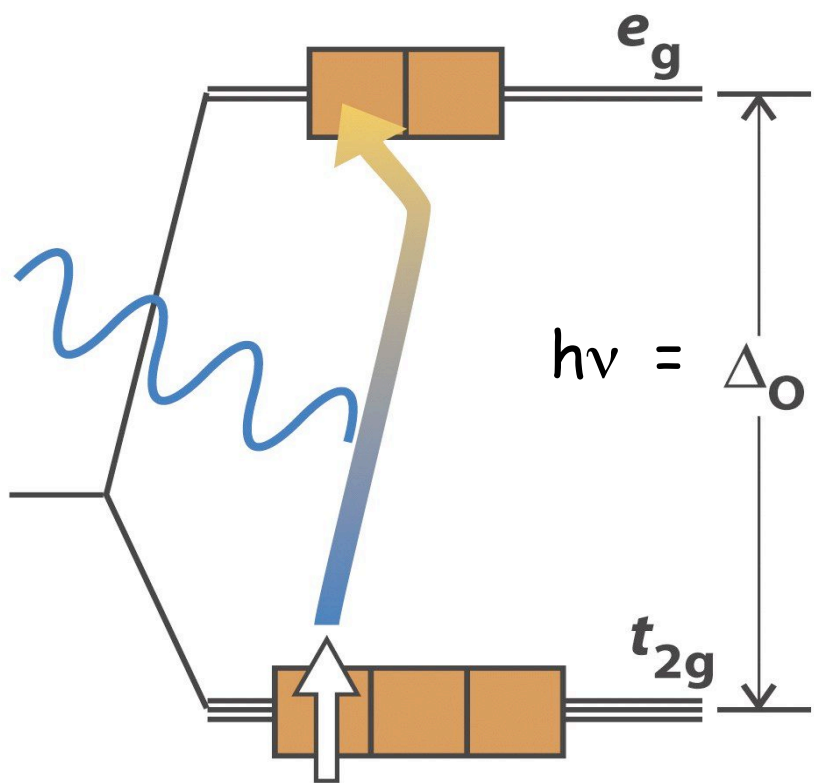


Energy gap small; Hund's rule applies

Electronic configuration of some $n+ d^n$ metal cations in octahedral complexes

Complex	Valence electrons	Unpaired electrons	Electron configuration	Spin configuration
$\text{Ti}(\text{H}_2\text{O})_6^{3+}$	$3d^1$	1	$(t_{2g})^1$	$(\uparrow)^1$
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	$3d^3$	3	$(t_{2g})^3$	$(\uparrow\uparrow\uparrow)^3$
$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	$3d^5$	5	$(t_{2g})^3(e_g)^2$	$(\uparrow\uparrow\uparrow)^3(\uparrow\uparrow)^2$
$\text{Fe}(\text{CN})_6^{3-}$	$3d^5$	1	$(t_{2g})^5$	$(\uparrow\downarrow\uparrow\downarrow\uparrow)^5$
$\text{Fe}(\text{H}_2\text{O})_6^{2+}$	$3d^6$	4	$(t_{2g})^4(e_g)^2$	$(\uparrow\downarrow\uparrow\uparrow)^4(\uparrow\uparrow)^2$
$\text{Fe}(\text{CN})_6^{2-}$	$3d^6$	0	$(t_{2g})^6$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6$
$\text{Ni}(\text{H}_2\text{O})_6^{2+}$	$3d^8$	2	$(t_{2g})^6(e_g)^2$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\uparrow)^2$
$\text{Cu}(\text{H}_2\text{O})_6^{2+}$	$3d^9$	1	$(t_{2g})^6(e_g)^3$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\downarrow\uparrow)^3$
$\text{Zn}(\text{H}_2\text{O})_6^{2+}$	$3d^{10}$	0	$(t_{2g})^6(e_g)^4$	$(\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow)^6(\uparrow\downarrow\uparrow\downarrow)^4$

19.4 Crystal Field Theory: The Color of Coordination Compounds



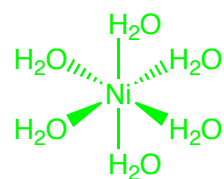
Absorption of a photon causes a jump from a t_{2g} to an e_g orbital

The energy gap between the e_g and t_{2g} orbitals, Δ_0 , (the crystal field splitting) equals the energy of a photon:

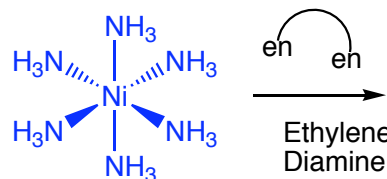
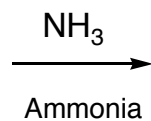
$$\Delta_0 = h\nu = \Delta E$$

As Δ_0 varies, $h\nu$ will also vary and the color of the compound will change

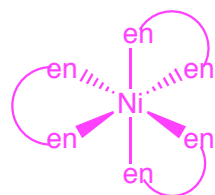
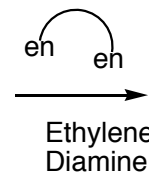
Ligand substitutions and color changes: Ni²⁺



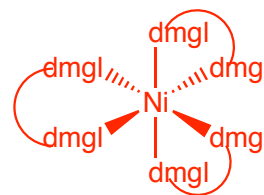
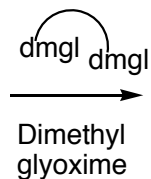
Green



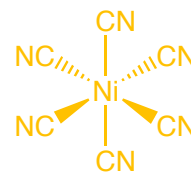
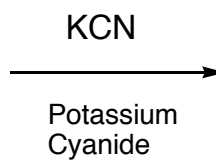
Blue



Purple



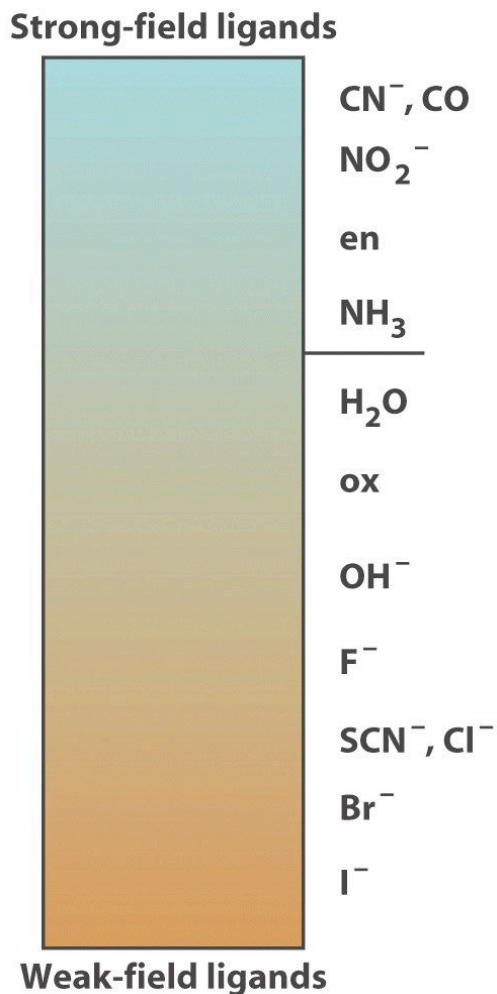
Pink



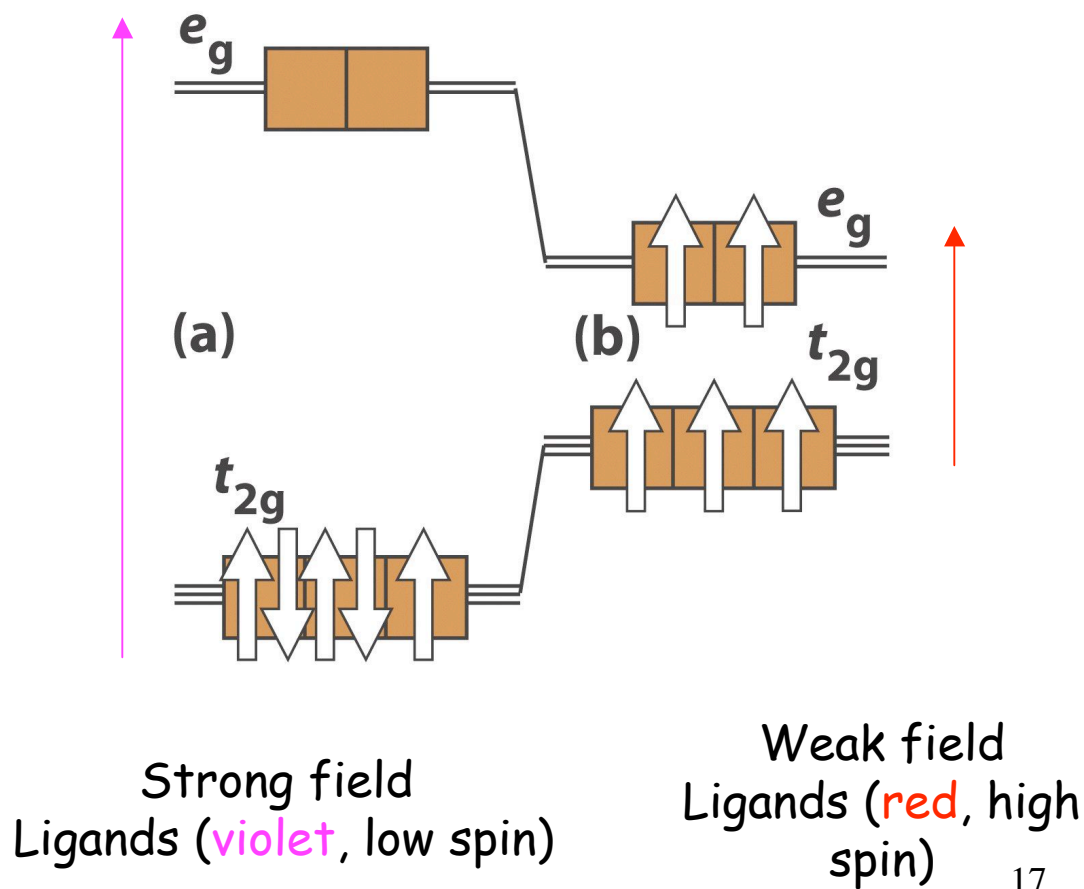
Yellow

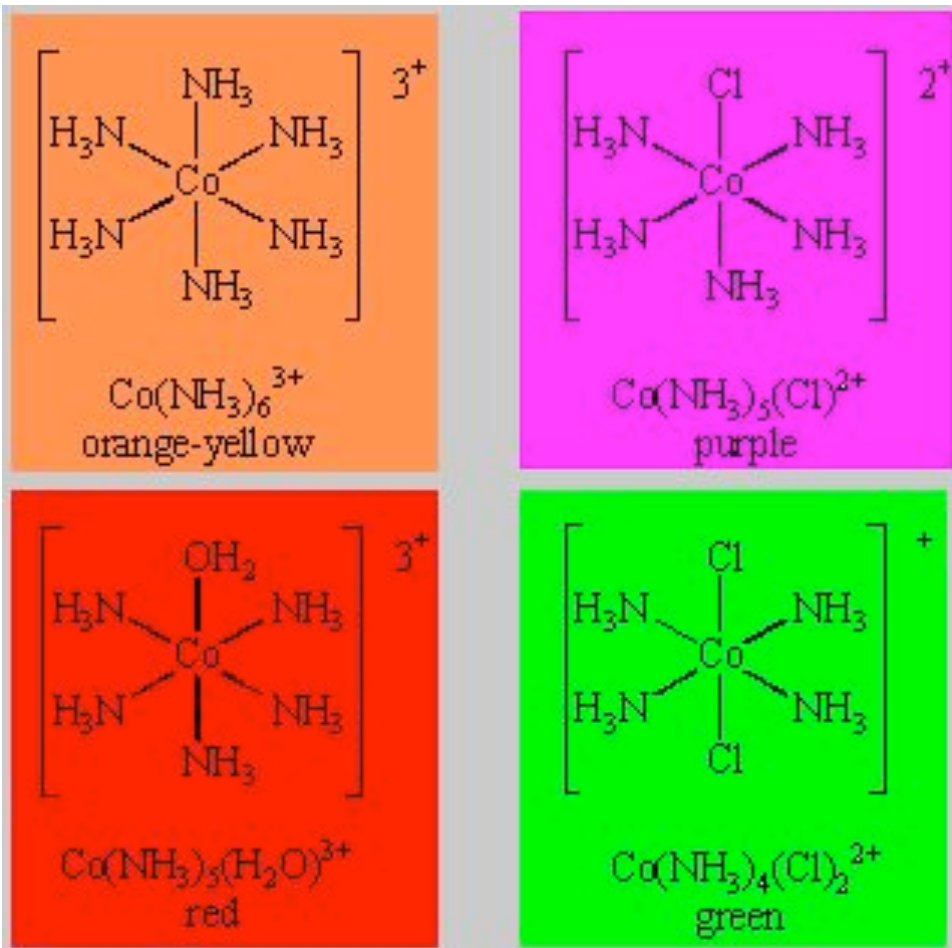
The spectrochemical series of color and magnetic properties:
 weak field (red, high spin), strong field (violet, low spin)

Spectrochemical series

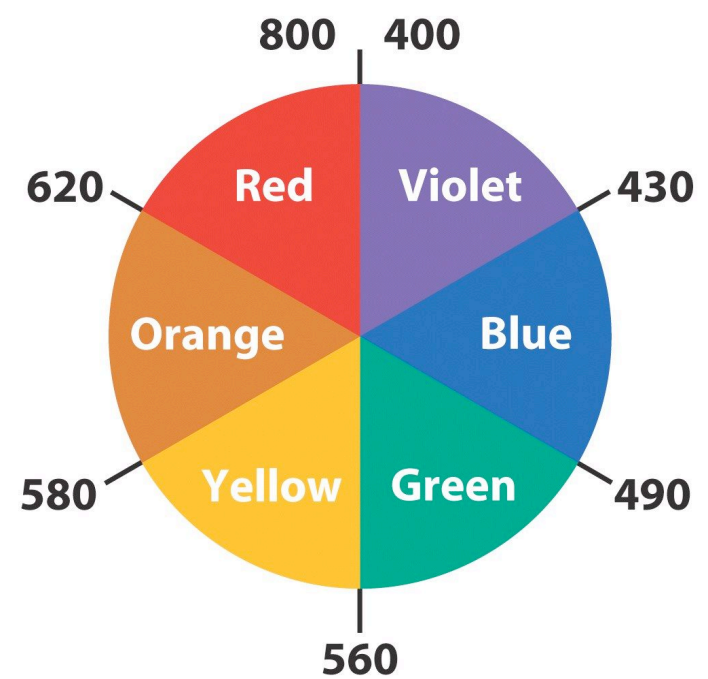


A d⁵ electron metal ion





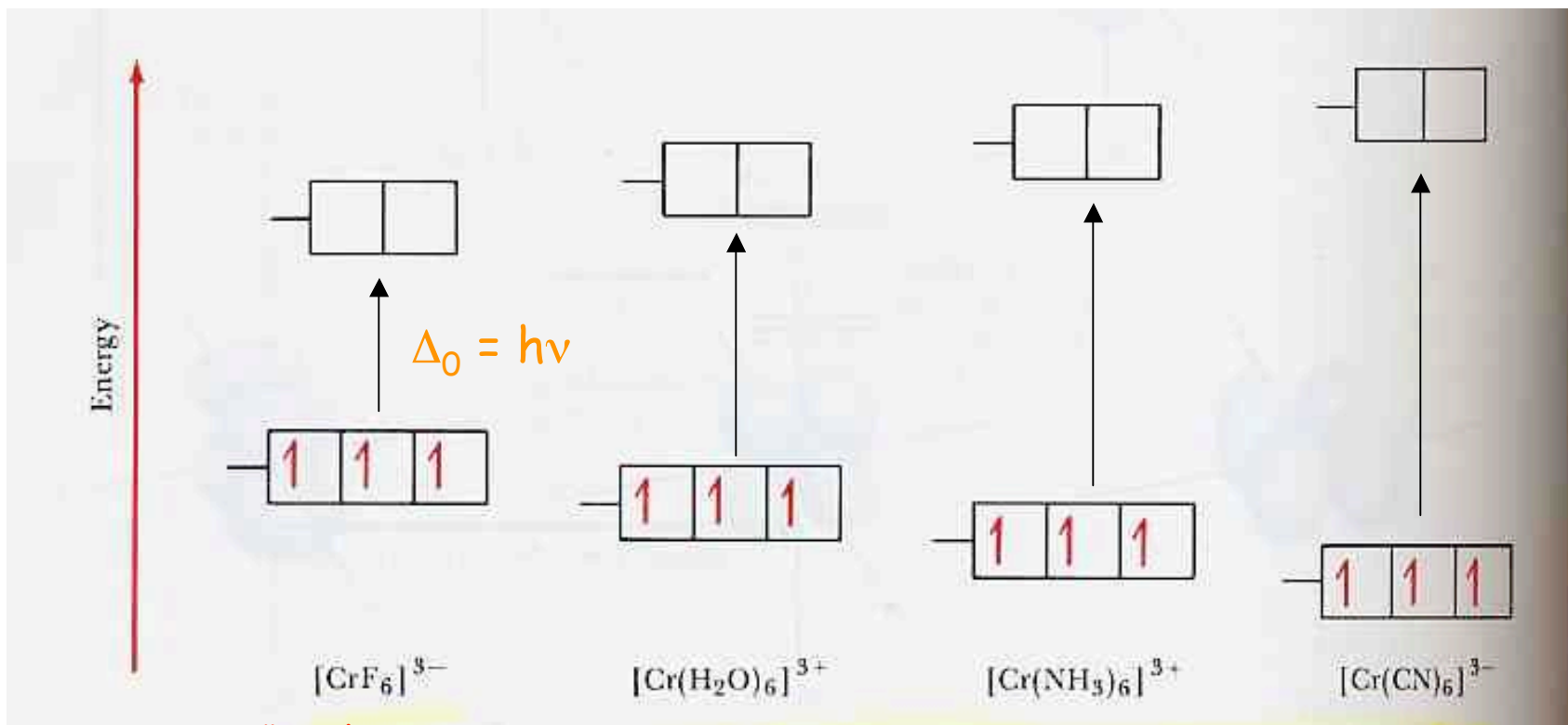
The color that we see is the color that is not absorbed, but is transmitted. The transmitted light is the complement of the absorbed light.



Numbers are nm

So if red light is mainly absorbed the color is green; if green light is mainly absorbed, the color is red.

Color of complexes depend on the value of $\Delta_0 = h\nu = \Delta E$

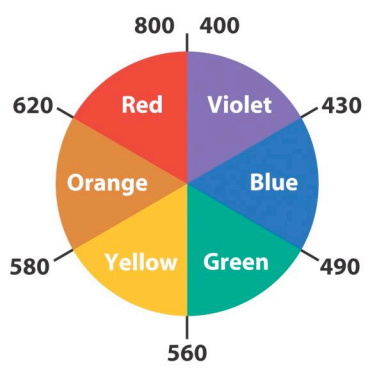


"red absorption"

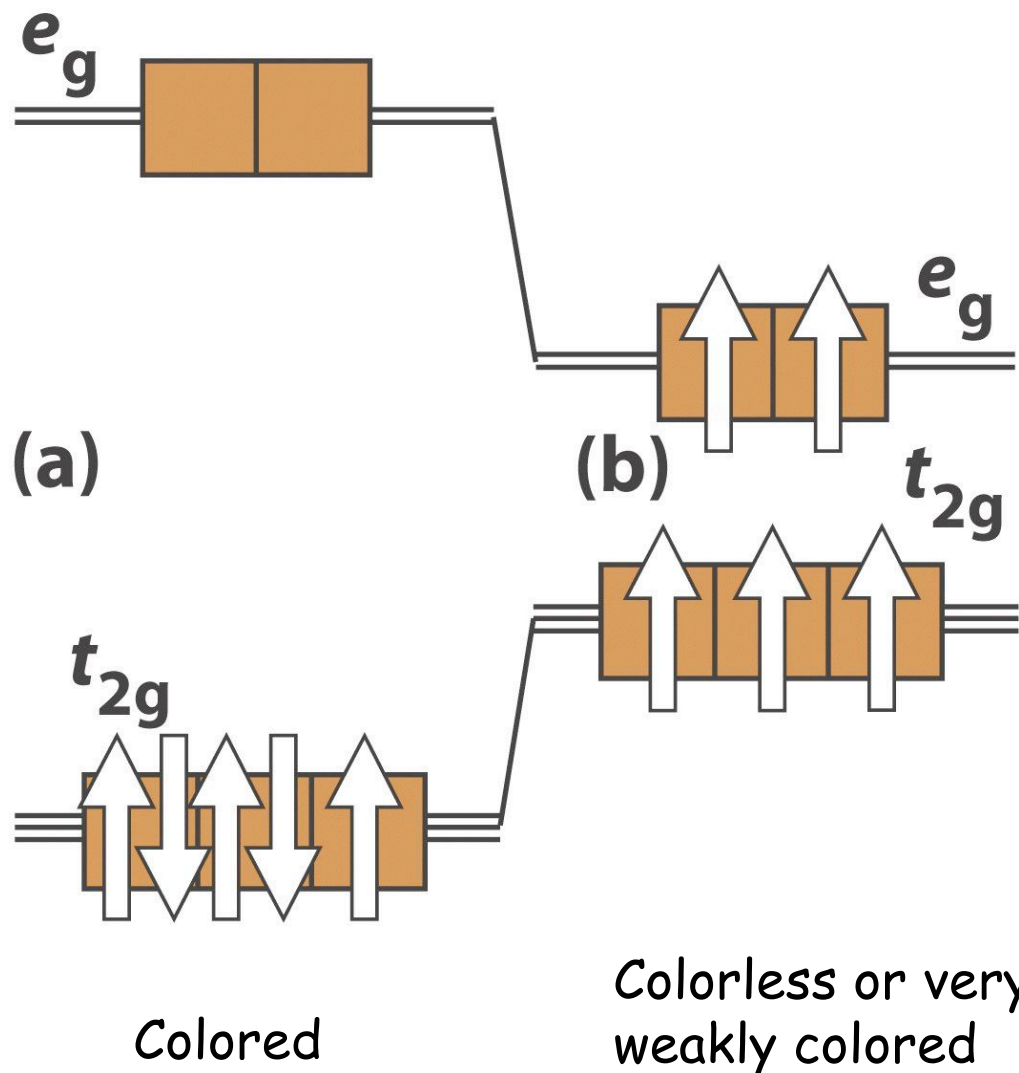
"looks green"

"violet absorption"

"looks yellow"



Crystal Field Splitting of d orbitals: high spin and low spin situations for a d^5 metal (why are some complexes colorless?)

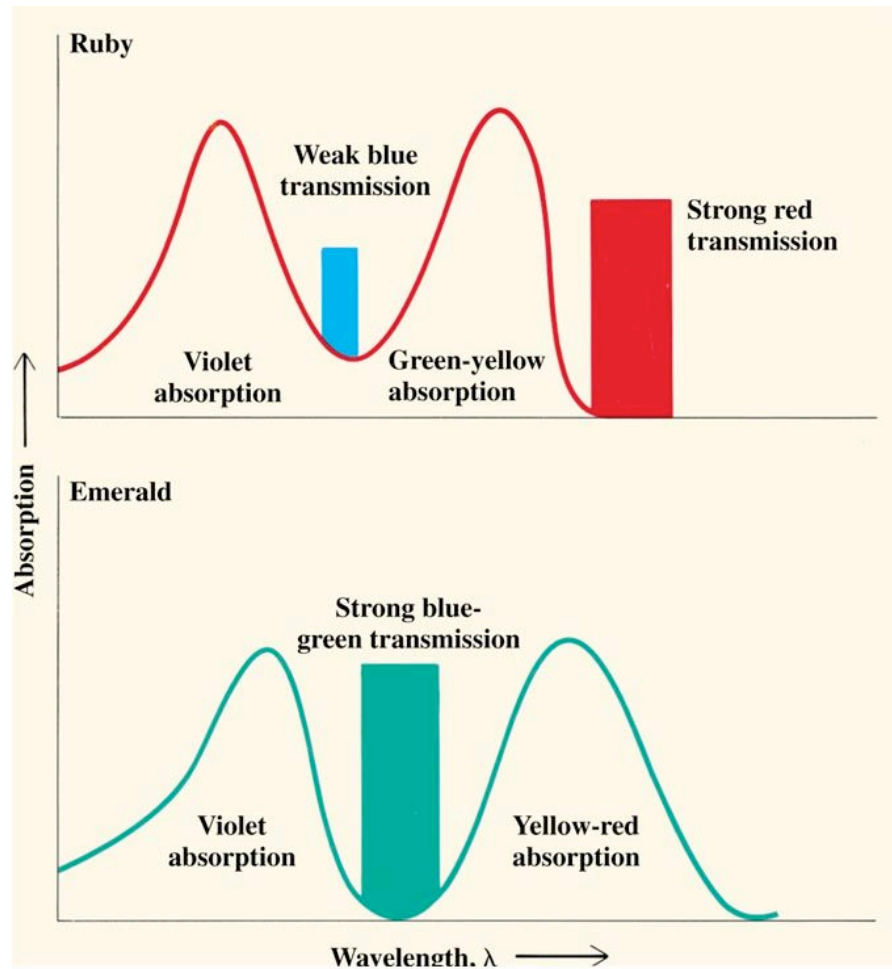


Color corresponds to the absorption of light and transitions between d orbitals for metals.

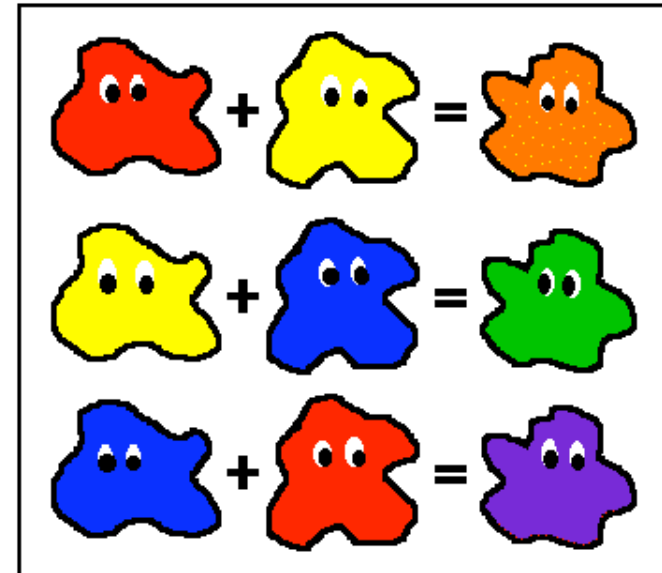
The transition for (b) is "spin forbidden" because an electron would need to "flip" its spin in being excited from a t orbital to a e orbital

Why?

Visualization of color as transmitted light which is not absorbed and the brain's perception of mixed colored



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In real systems there are regions of different light absorptions leading to a wide range of colors

19.5 Coordination Complexes in Living Systems

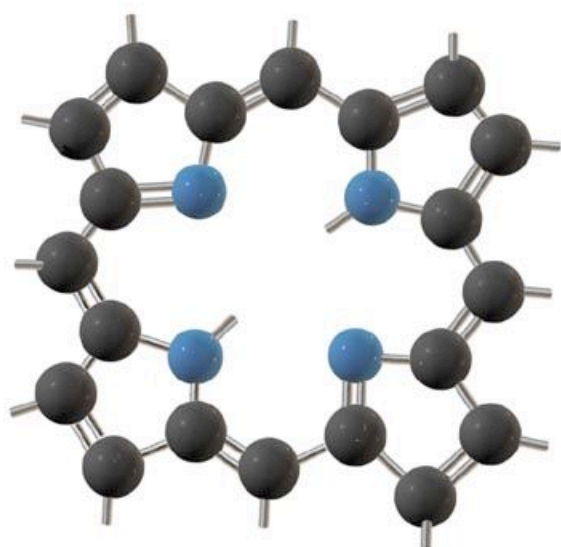
Porphines, hemes, hemoglobin

Photosynthesis: electron transfer

Vitamin B₁₂

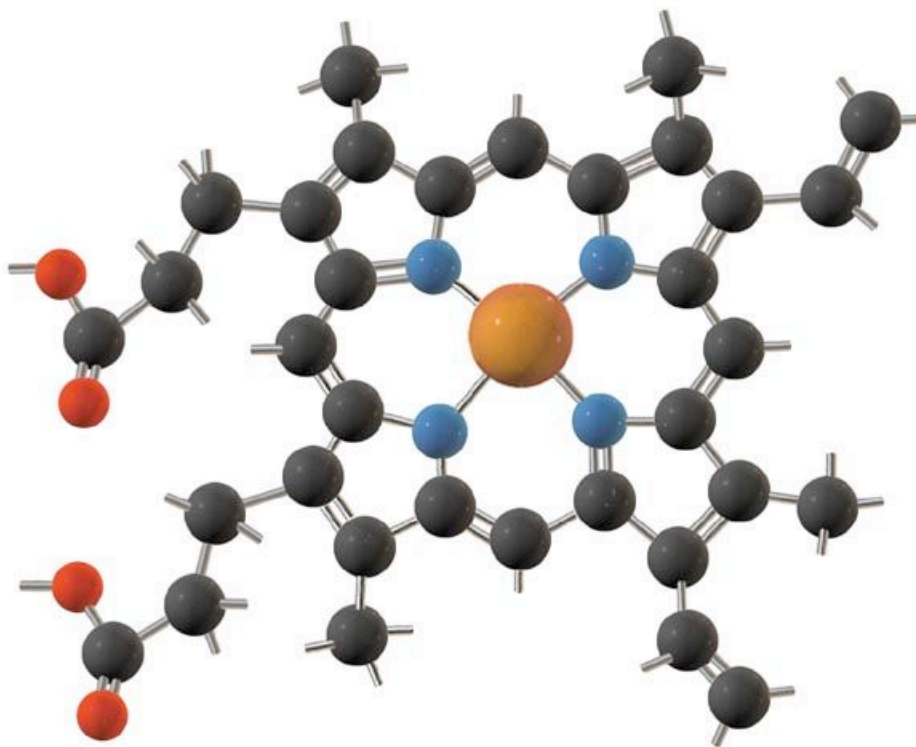
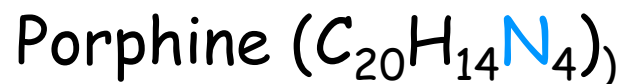
Porphines and hemes: important molecules in living systems

These planar molecules have a "hole" in the center which to which a metal can coordinate

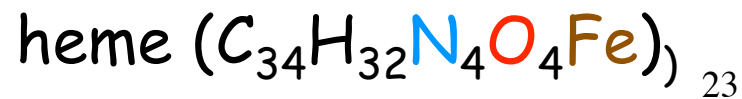


[a]

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[b]



Why do we need to eat d metals?

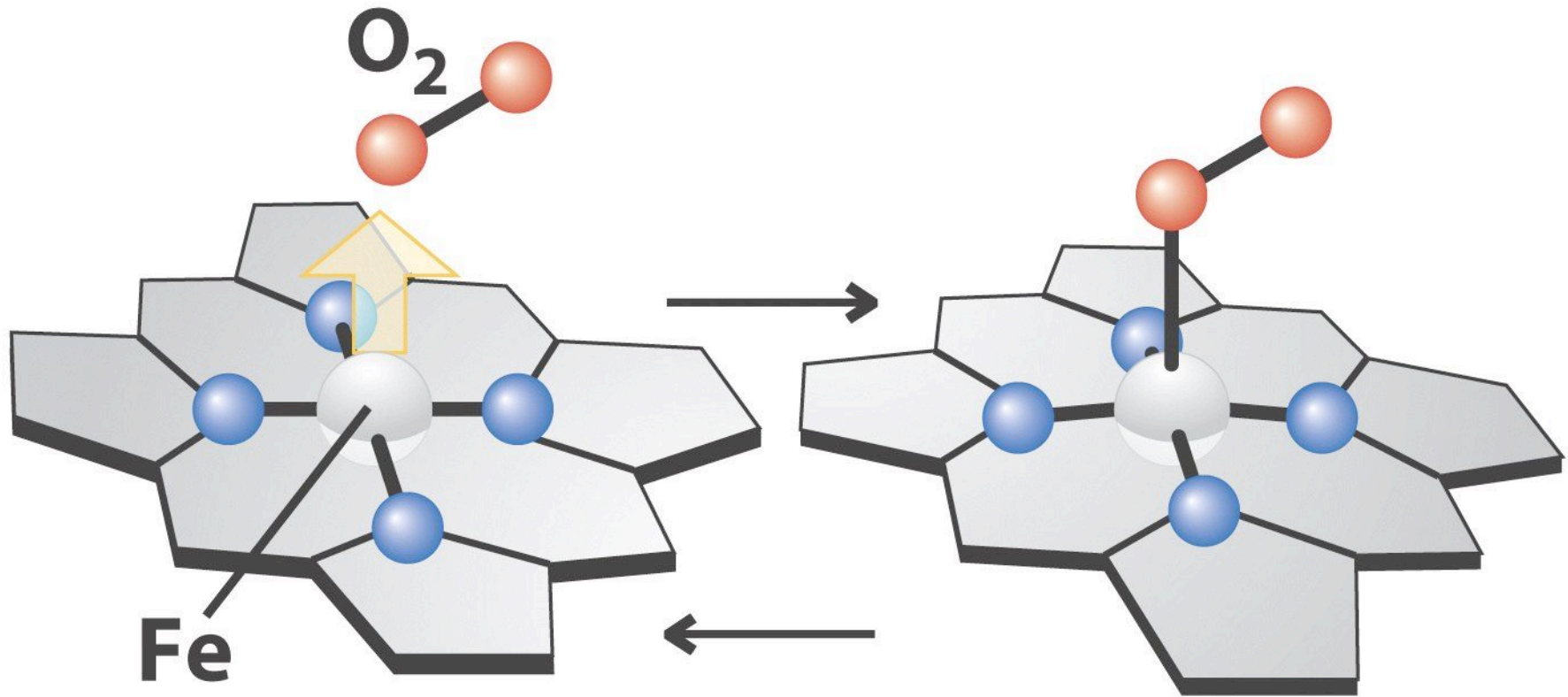
Some critical enzymes in our cells are *metalloproteins*, giant biomolecules which contain a metal atom

These metalloproteins control key life processes such as respiration and protect cells against disease

Hemoglobin is a metalloprotein which contains an iron atom and transports O_2 through out living systems

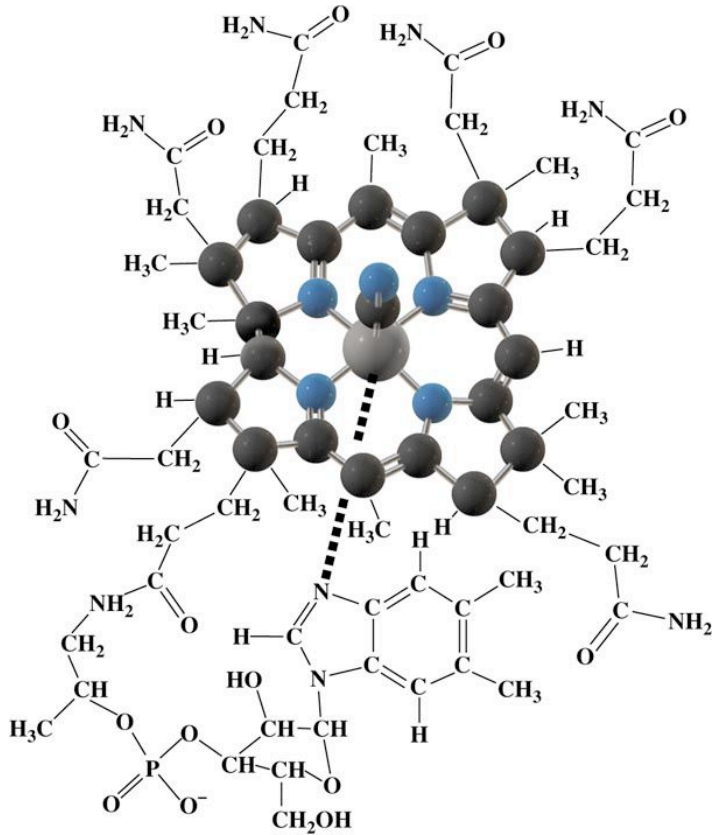
Vitamin B_{12} , which prevents pernicious anemia, contains a Co atom which gives the vitamin a red color

Reversible addition of O_2 to hemoglobin

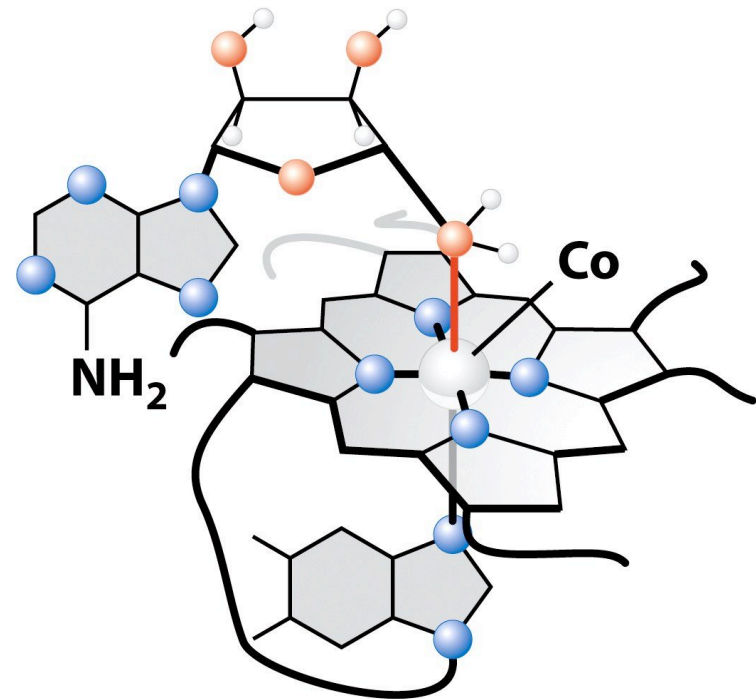


The mechanism by which oxygen is carried throughout the body

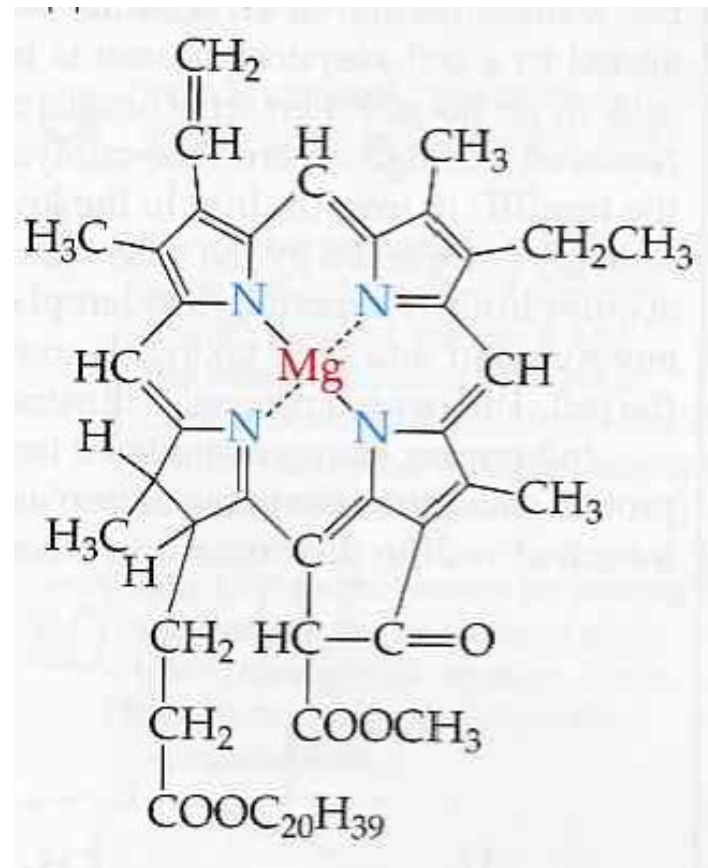
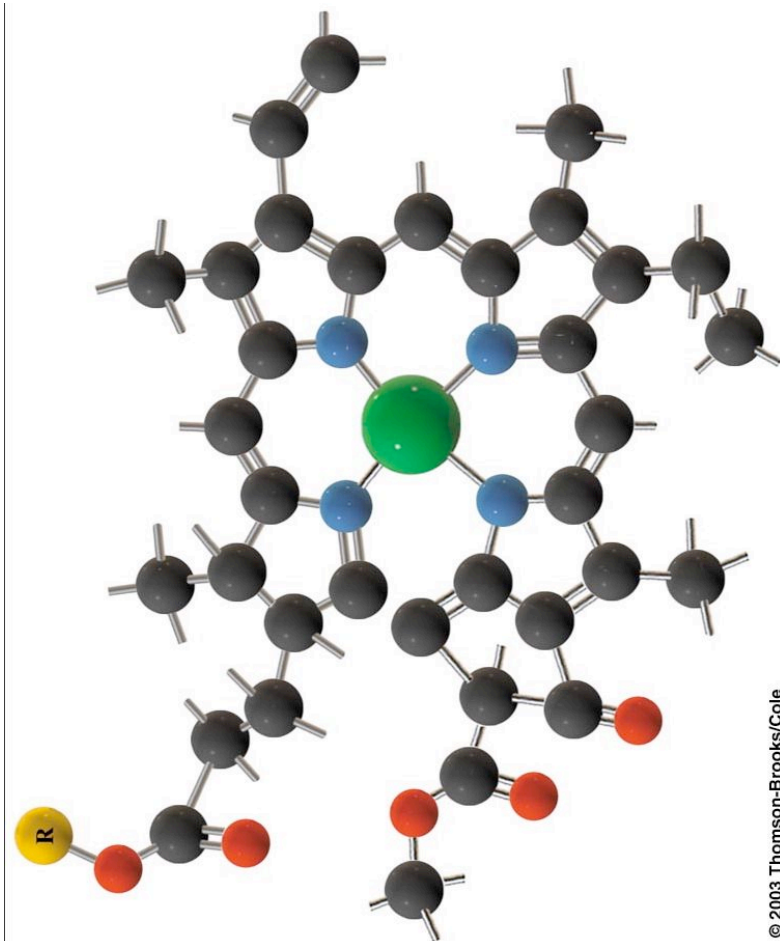
Involved in many important biological processes,
including the production of red blood cells



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A very important porphine that converts solar photons into food energy: chlorophyll



Chlorophyll ($\text{C}_{55}\text{H}_{72}\text{N}_4\text{O}_5\text{Mg}$)