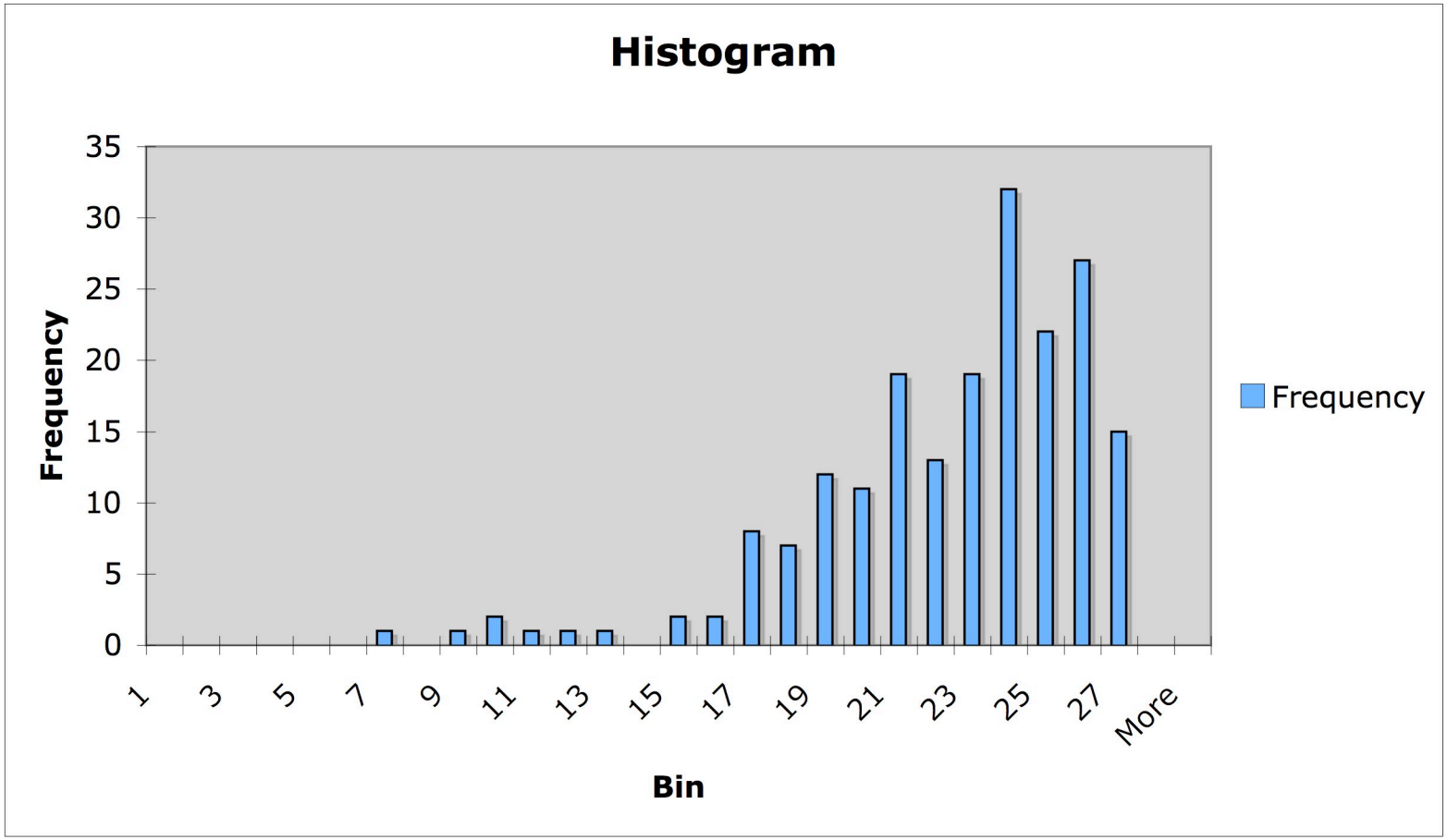
Frequency of scores on exam 2

Grade = n(right)/28 x 100



Photochemistry and biology

Photons can be toxic (cause DNA bases to dimerize)

Photons can be therapeutic: phototherapy

Photons can track thoughts, one molecule at a time (Chapter 25)

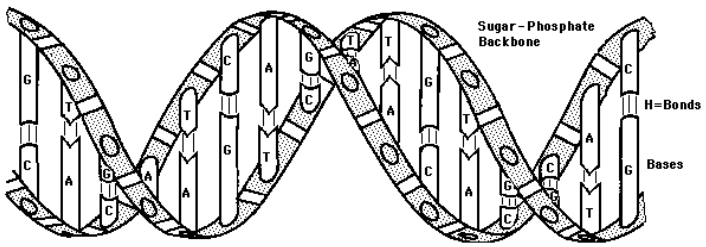
Photons can image whole bodies and search for disease (Chapter 25)

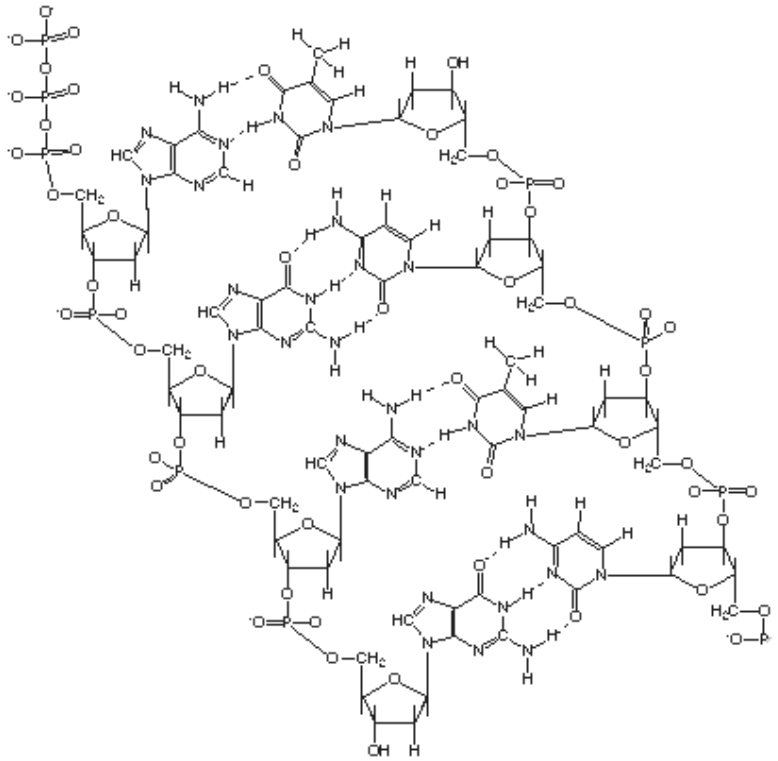
The Central Dogma of Chemical Biology

Biology is chemistry in action!

Phototoxicity: Damage to DNA

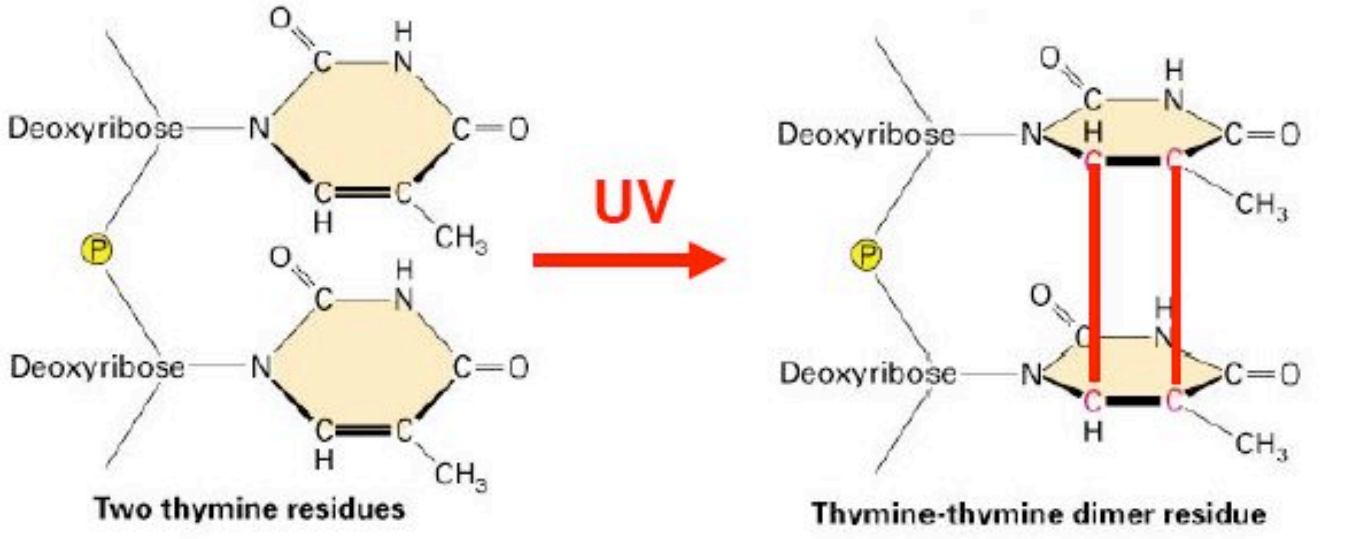
- DNA
- 2' ***D***eoxyribo ***N***ucleic ***A***cid





DNA: UV photochemistry

Thymidine dimers are generated by exposure to UV light

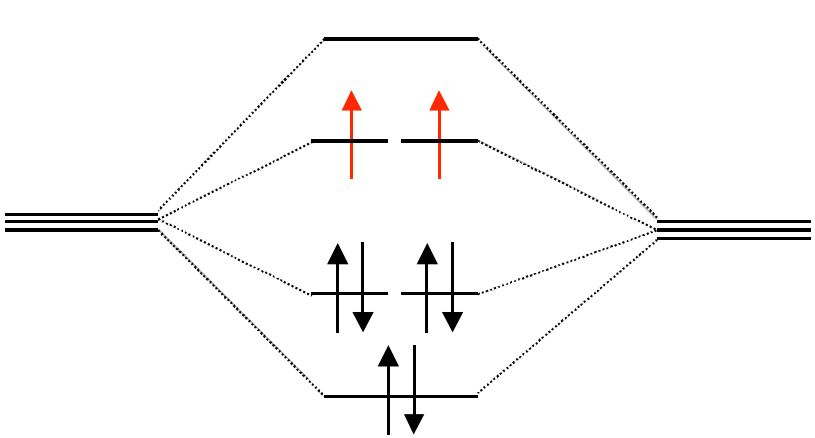


Two DNA bases lined together

Photons cause two DNA bases to link: this kills the cells containing the irradiated DNA

Singlet molecular oxygen: excited states of ordinary oxygen

The Aufbau of the MOs of O_2



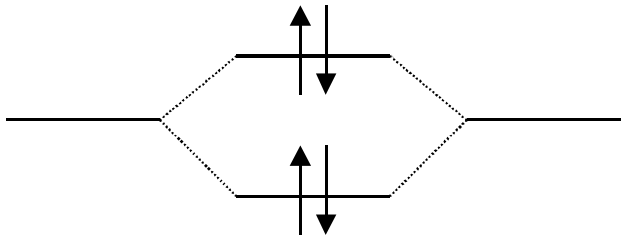
$3\sigma_u^*$

$1\pi_g^*$

$1\pi_u$

$3\sigma_g$

2p

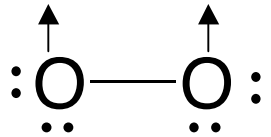


$2\sigma_u$

$2\sigma_g$

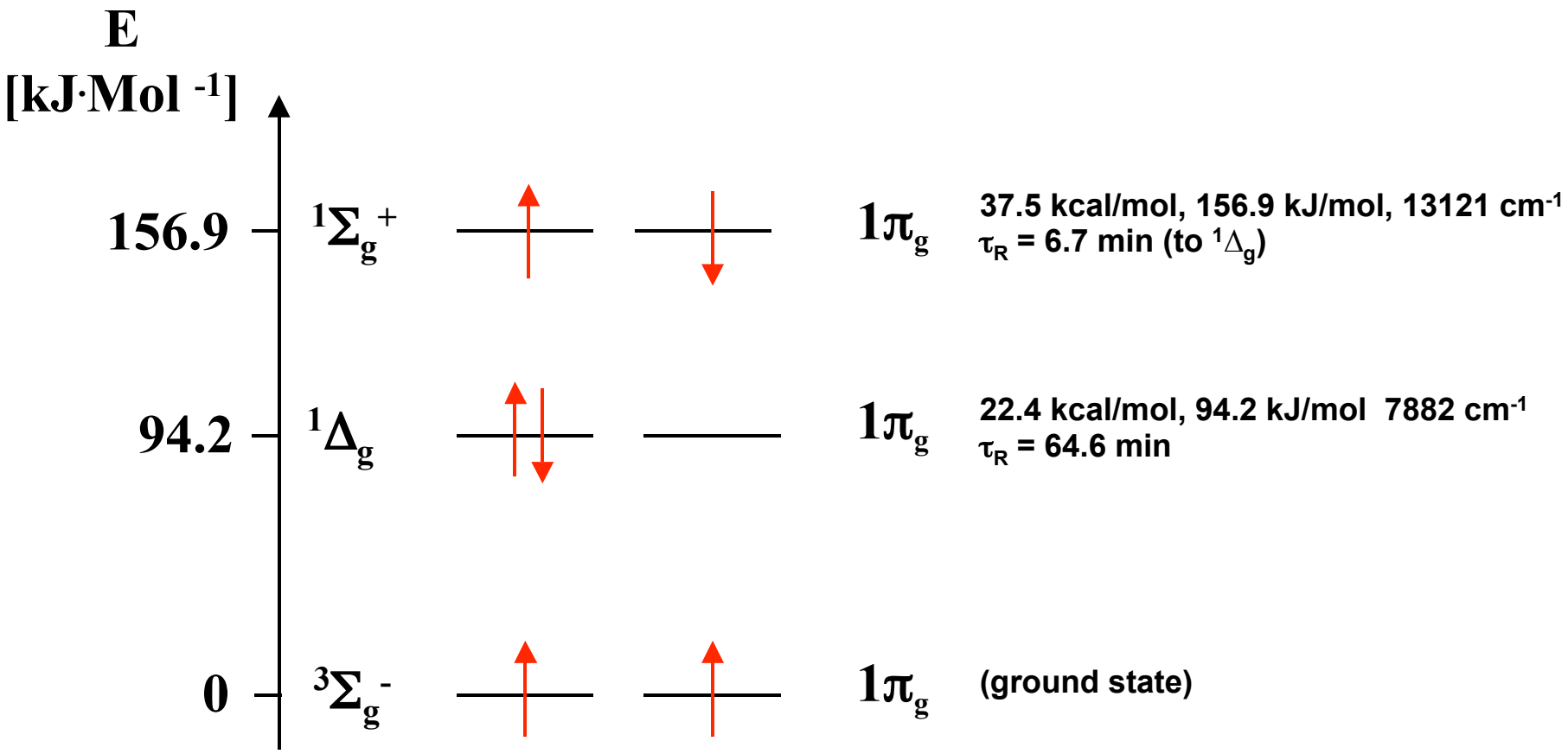
2s

Hund's rule states: When there are two electrons to be placed in two orbitals of equal energy, the lowest energy configuration places one electron in each orbital with parallel spins, a triplet state

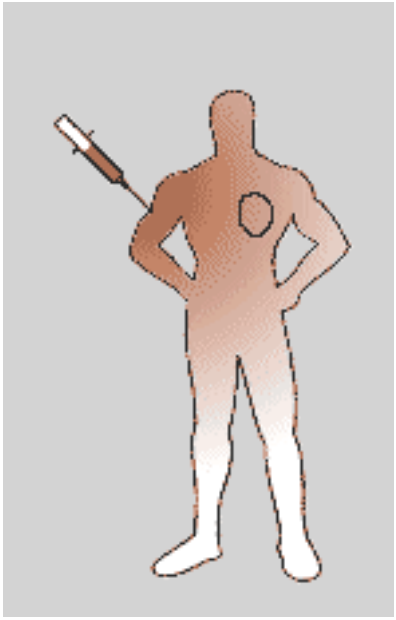


Electronic states of molecular oxygen: two low lying spin paired singlet states

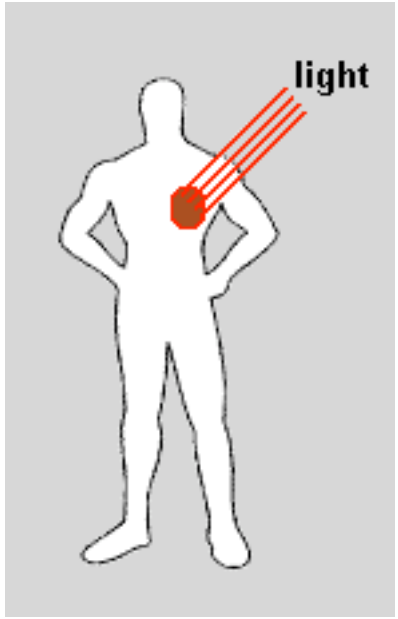
The singlet states of O_2 can kill cancer cells (and other cells)



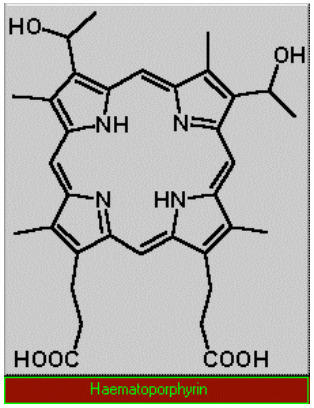
Photodynamic therapy using singlet oxygen



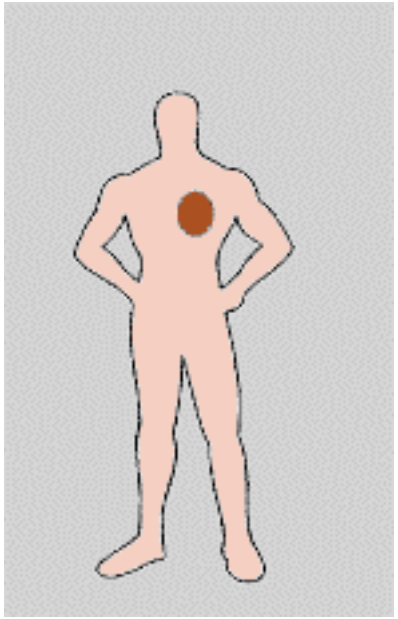
Porphyrin injected into patient



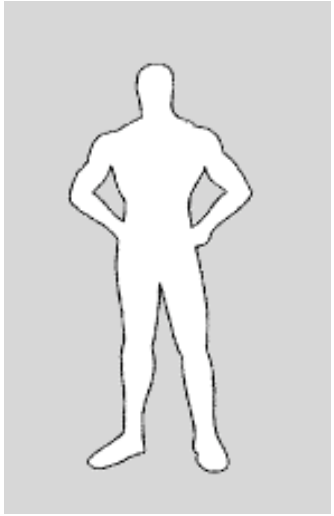
Only the affected organ irradiated with light



(Abs 390 - 450 nm)



$^1O_2$ kills cancer cells in irradiated area

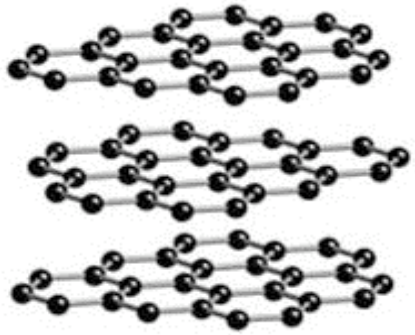


Patient cured!

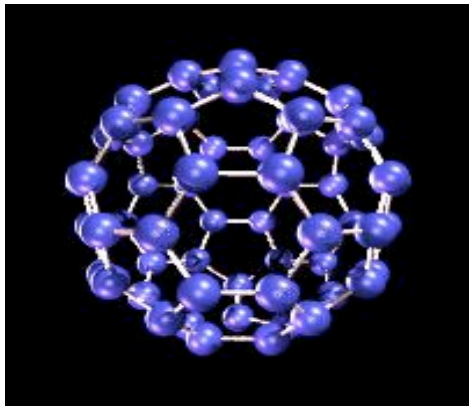
Irradiating babies with jaundice causes a photochemical change that causes the jaundice pigment to become water soluble and to be excreted

Different forms of elemental carbon: from diamond to graphite to ***buckyballs***!

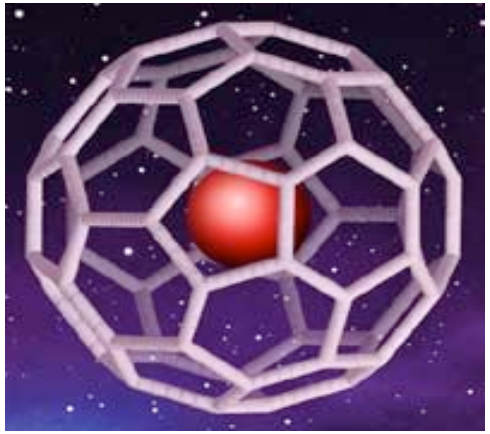
Diamond



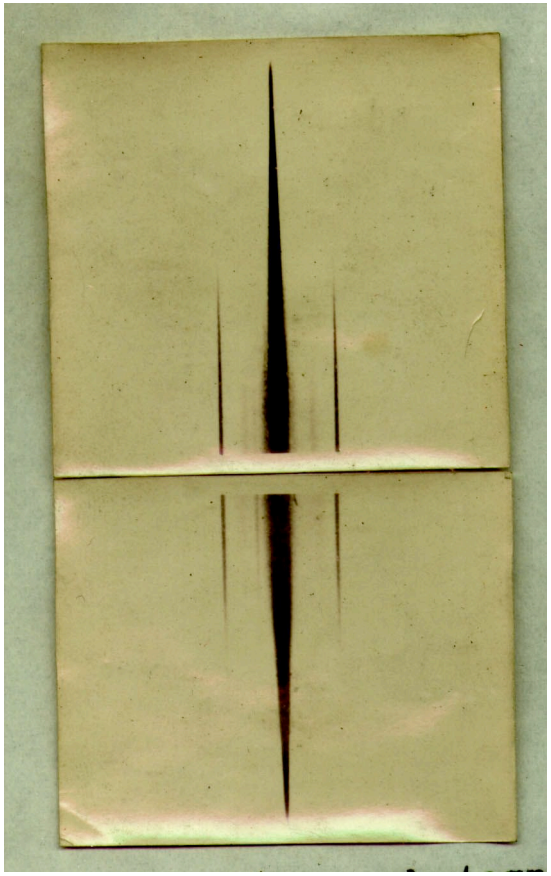
Graphite

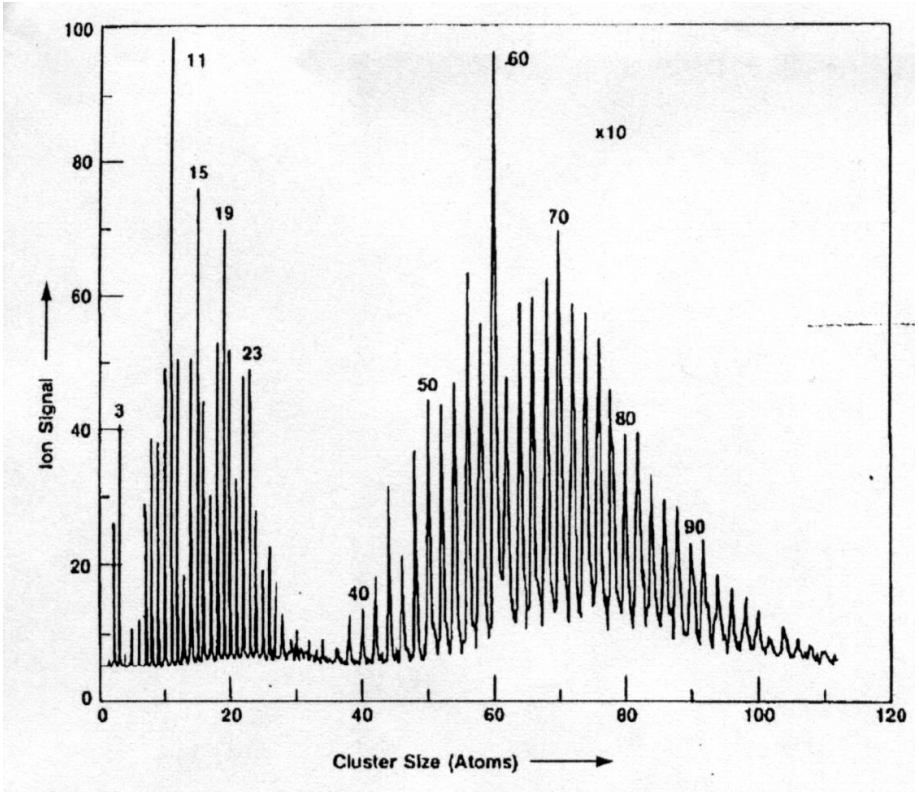


C_{60}



$H_2@C60$

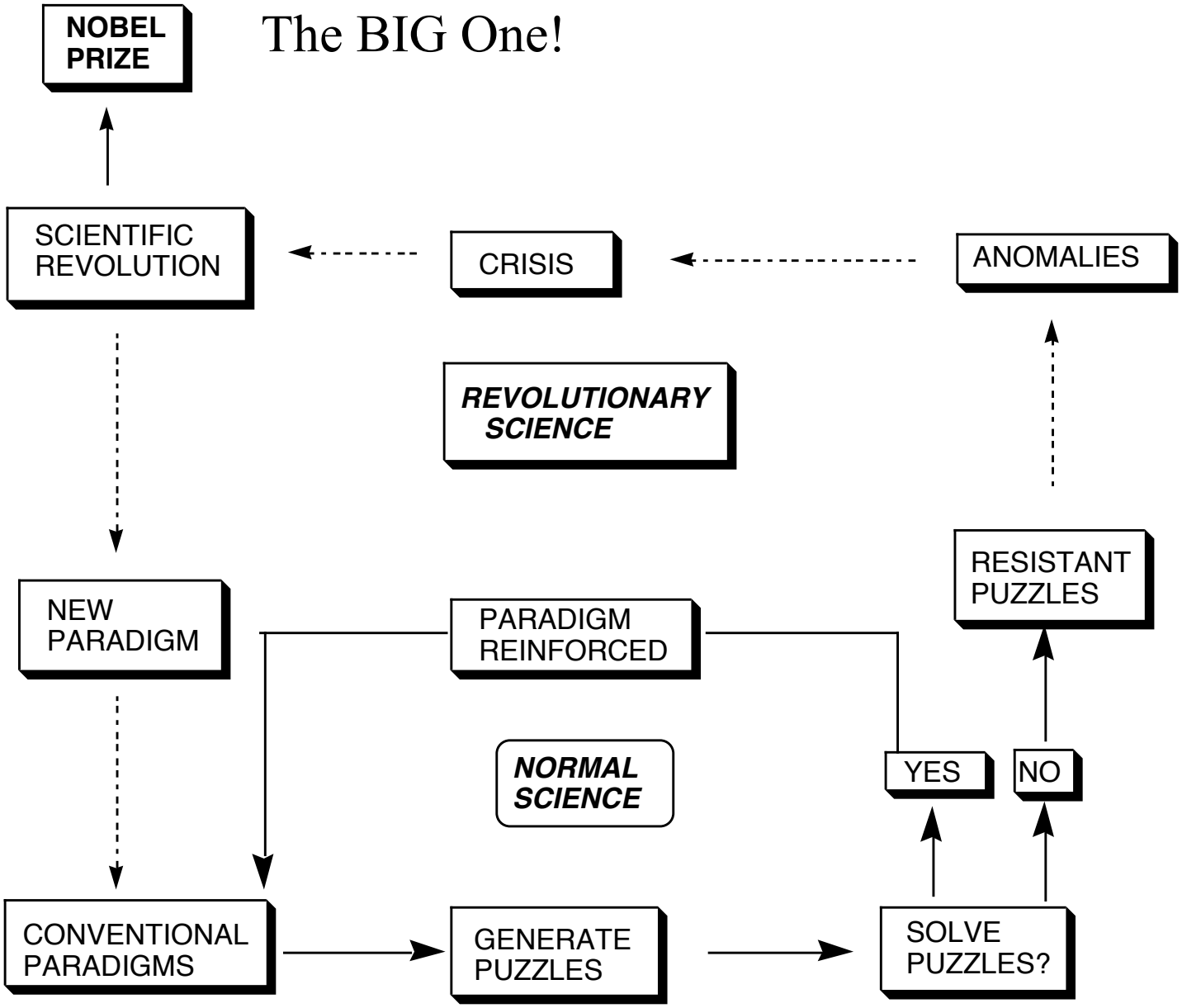




Discovery of Deuterium
Nobel Prize: 1934

Discovery of C_{60}
Nobel Prize: 1996

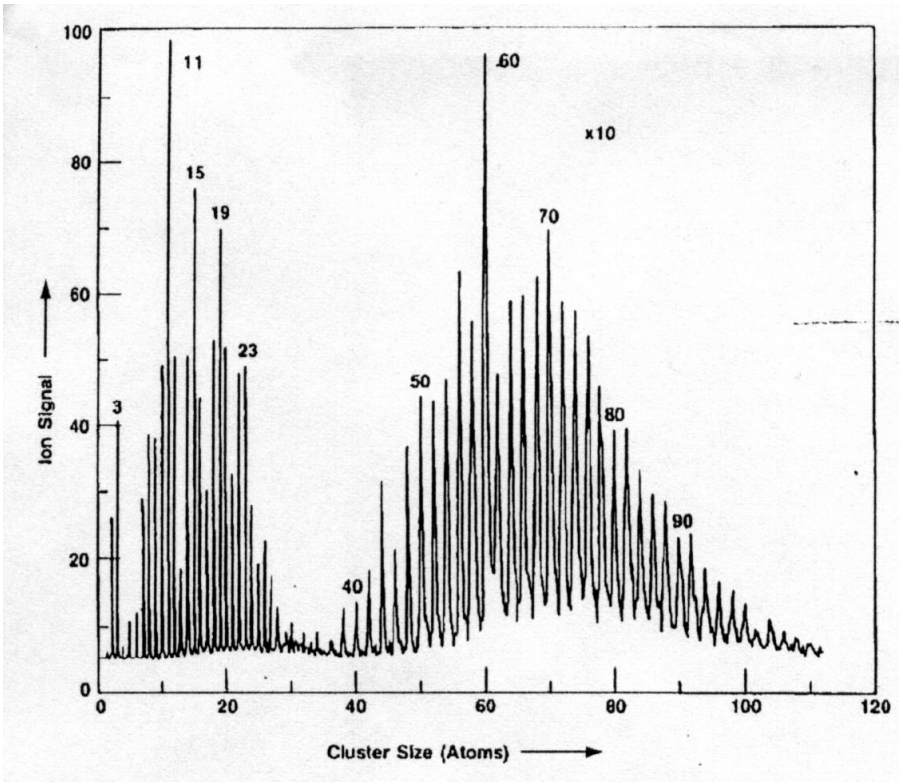
The BIG One!



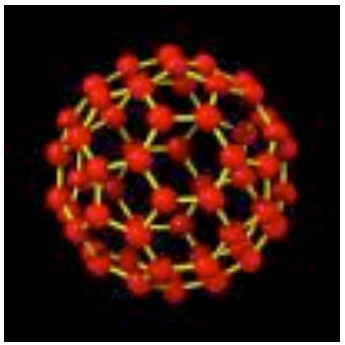
Flow diagram for revolutionary science:Extraordinary claims that become accepted and are integrated into "normal science."

An Extraordinary Claim: Carbon can exist in an elemental form that has a structure reminiscent to a soccer ball.

The first "evidence" for the special stability of C_{60}

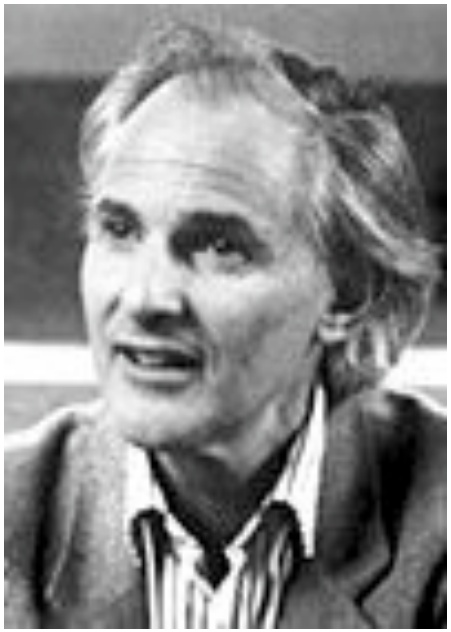


Discovery of C_{60} "Buckyballs" Pathological Science or Revolutionary Science?



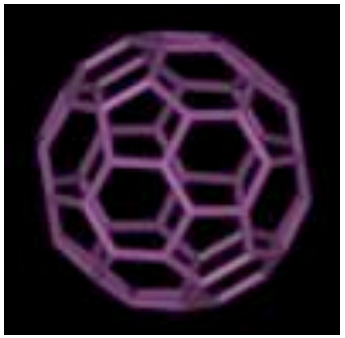
Would you have predicted a Nobel Prize?

Robert Curl



Harold Kroto

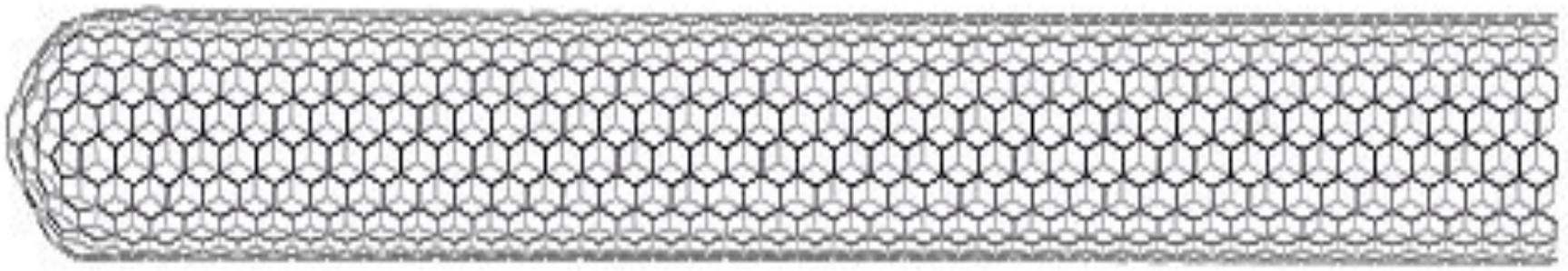
Richard Smalley

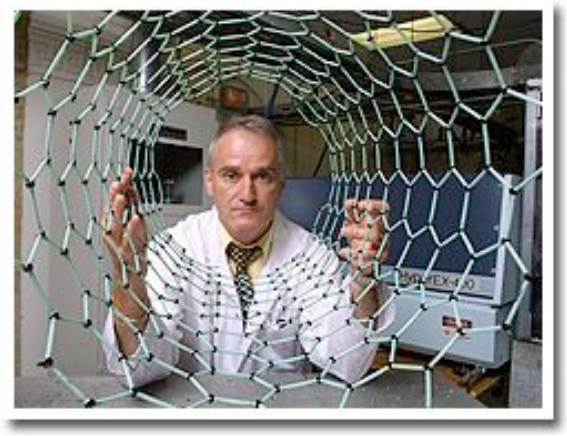


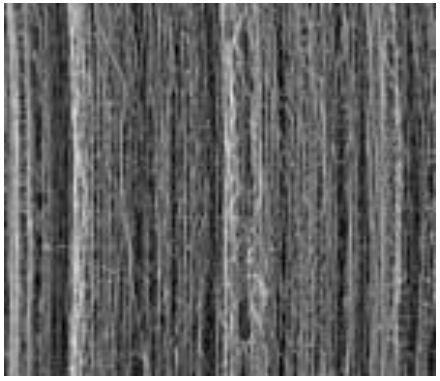
The Nobel Prize in Chemistry 1996
"for the discovery of fullerene"

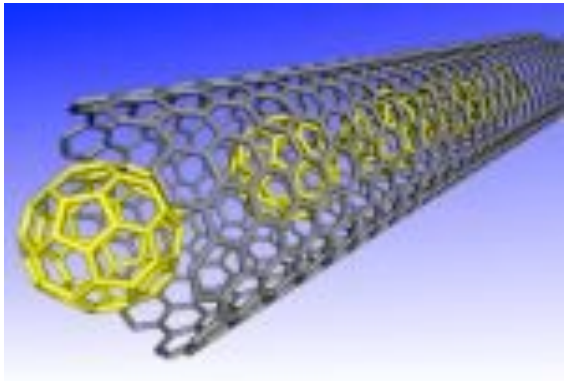
The proposal of Buckeyballs turned out to be *revolutionary* science

Buckyballs pulled into nanowires: Carbon nanotubes!

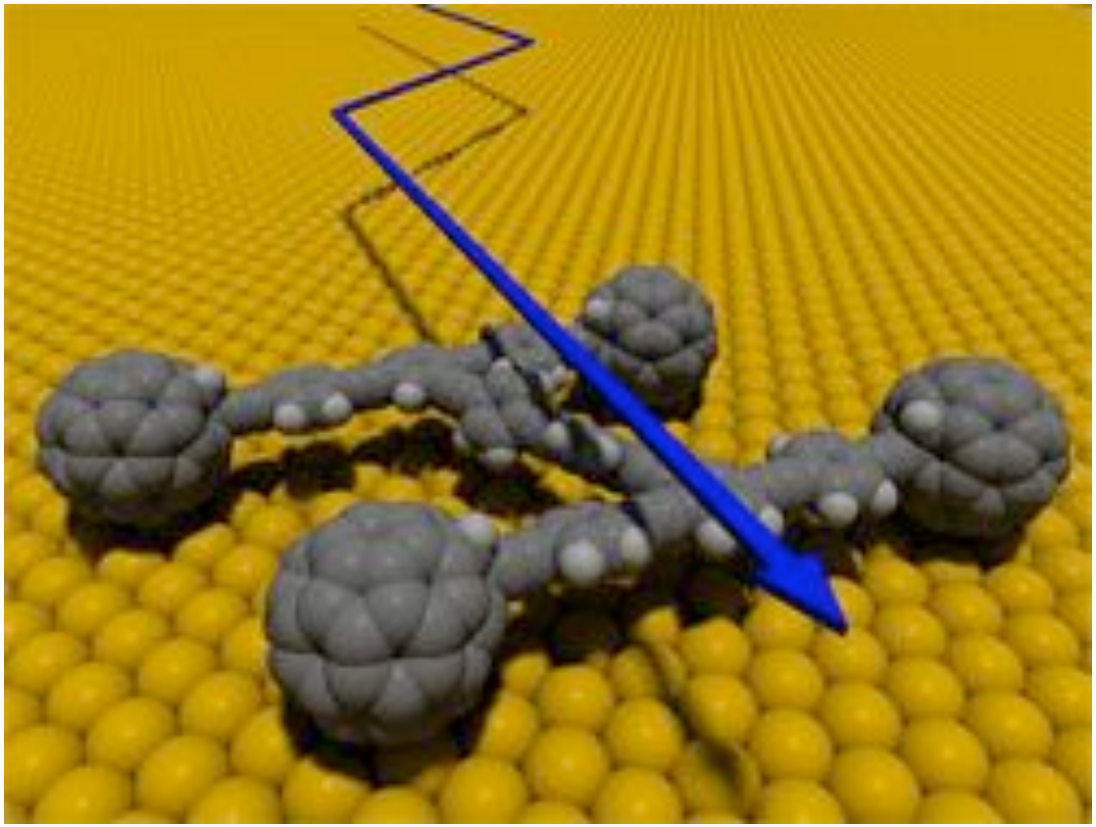






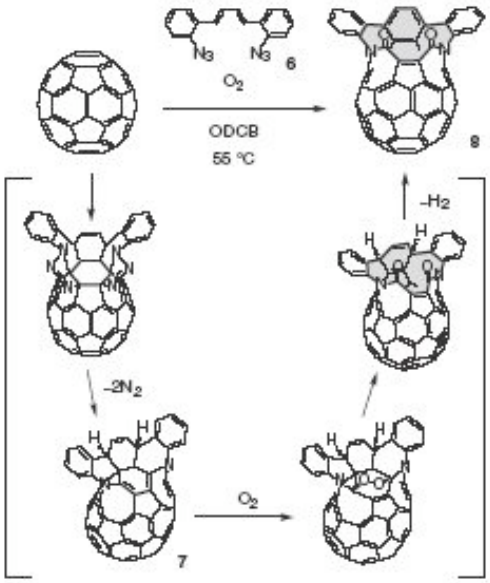


Nanodevices: A carbon nanocar rolling on a gold surface

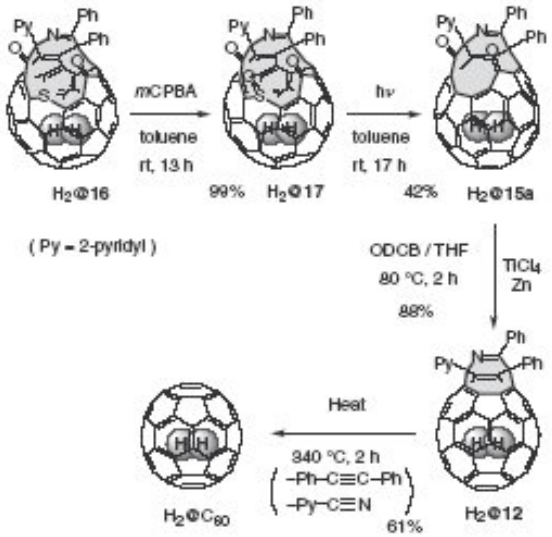


Thanks to Whitney Zoller

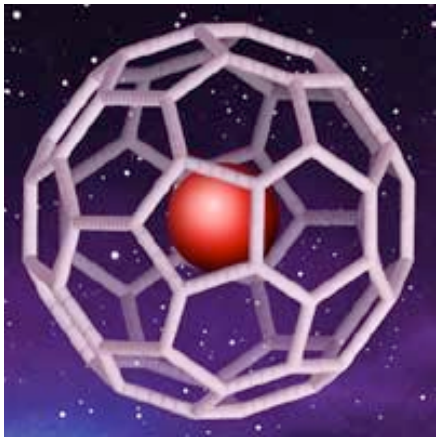
Putting H_2 inside a buckyball!



Open the buckyball



Put in H2, then close buckyball



H_2@C60

Collaborator: Professor Koichi Komatsu (Kyoto University)

C1403 Lecture 19 Monday, November 14, 2005

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

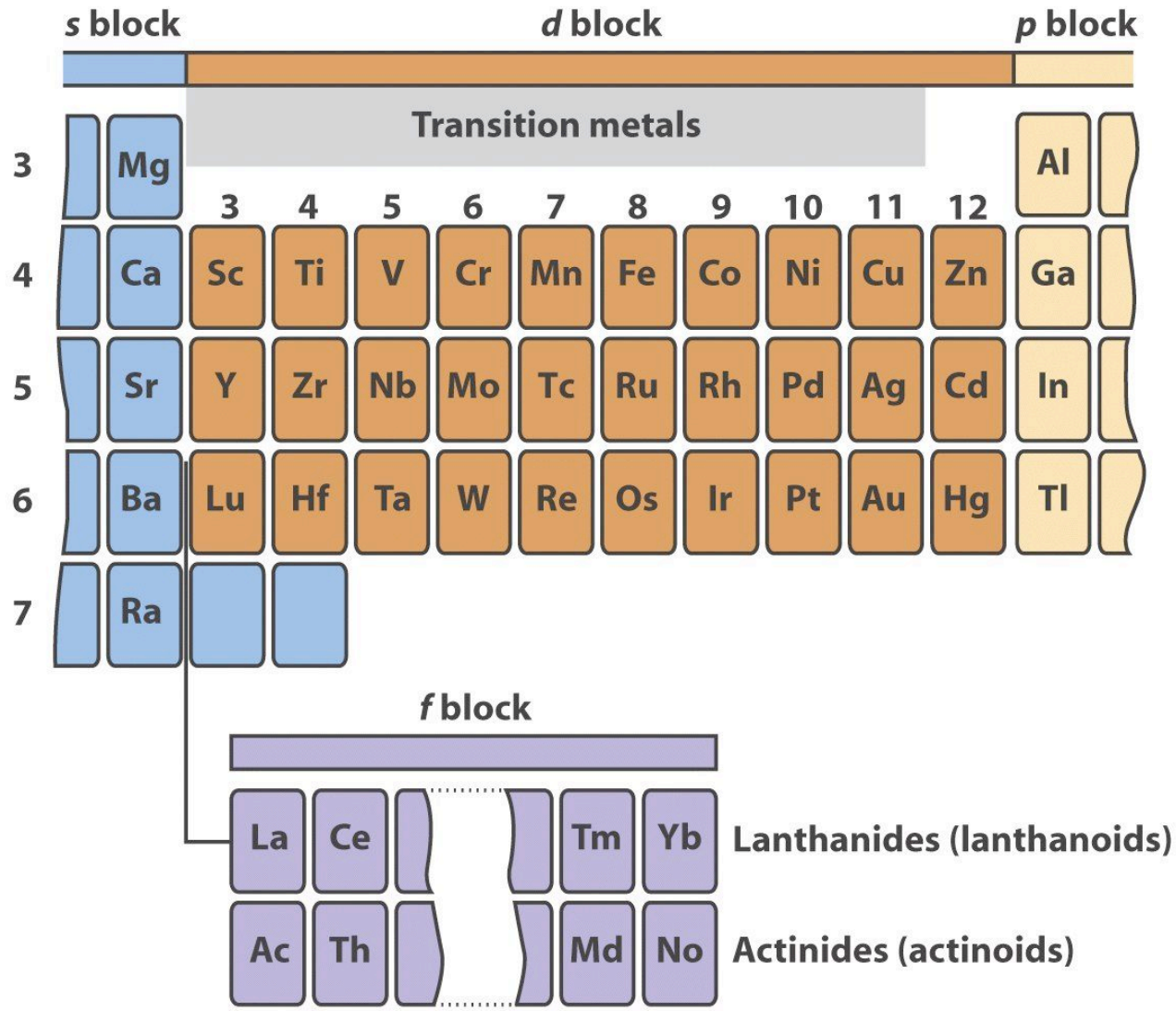
Infrared spectroscopy (IR tutor)

Chapter 24	**From Petroleum to Pharmaceuticals**
24.1	Petroleum Refining and the Hydrocarbons
24.2	Functional Groups and Organic Synthesis
24.3	Pesticides and Pharmaceuticals

Nuclear magnetic resonance spectroscopy

Chapter 25	**Synthetic and Biological Polymers**
25.1	Making Polymers
25.2	Biopolymers
25.3	Uses for Polymers

The d block metal form ***coordination complexes*** with molecules and ions



19.1 Coordination complexes

What is the electronic basis of the color of metal complexes?

Coordination complex: A structure containing a **metal** (usually a metal ion) bonded (coordinated) to a group of surrounding **molecules or ions**.

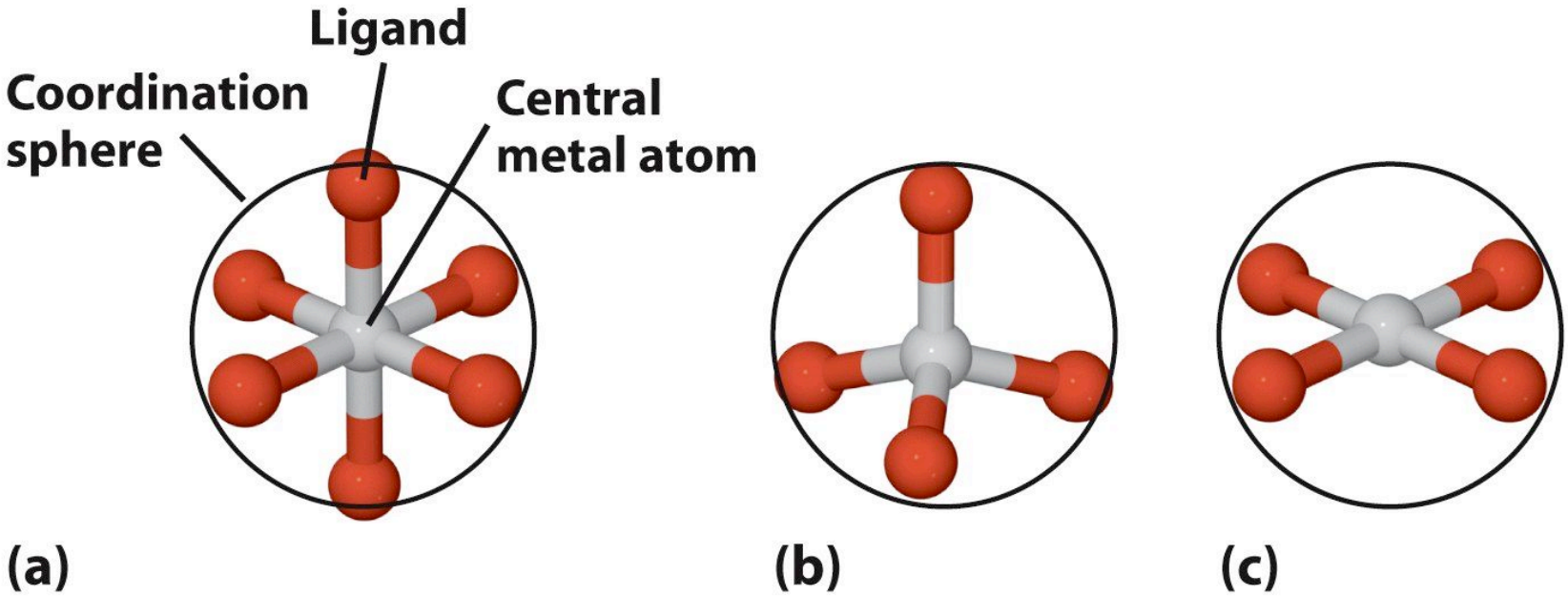
Ligand (ligare is Latin, to bind): A ligand is a molecule or ion that is directly bonded to a metal ion in a coordination complex

A ligand uses a **lone pair of electrons** (Lewis base) to bond to the metal ion (Lewis acid)

Coordination sphere: A metal and its surrounding ligands

Note: religion is derived from Latin: religare, to bind tightly

Complex ions: Three common structural types



Octahedral:
Most important

Tetrahedral

Square planar

What determines why a metal takes one of these shapes?

Lewis acids and bases

A Lewis base is a molecule or ion that donates a lone pair of electrons to make a bond

Examples: $:NH_3$ $:OH_2$ $:Cl^-$ $:F^-$

Electrons in the highest occupied orbital (HO) of a molecule or anion are the best Lewis bases

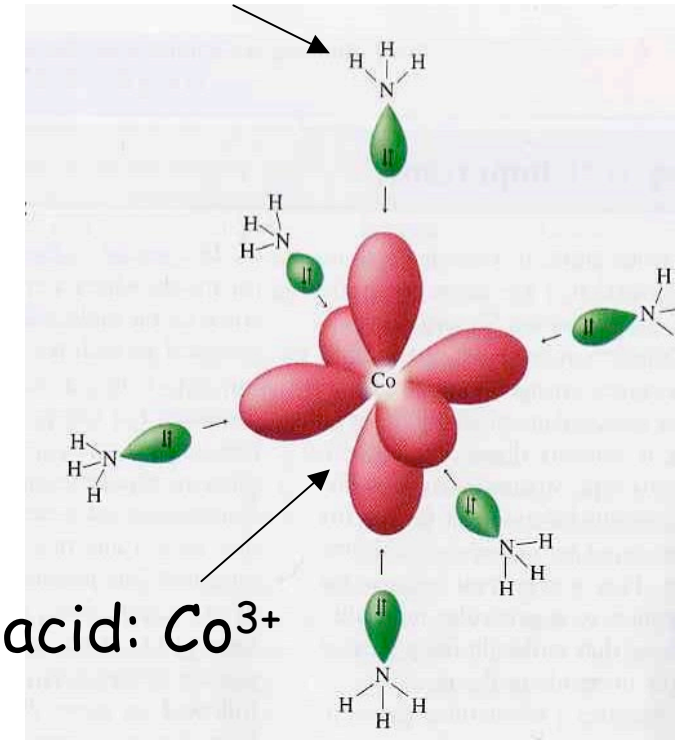
A Lewis acid is a molecule of ion that accepts a lone pair of electrons to make a bond

Examples: H^+ Co^{3+} Co^{2+} M^{n+}

Molecules or ions with a low lying unoccupied orbital (LU) of a molecule or cation are the best Lewis acids

The formation of a coordinate complex is a ***Lewis acid-base*** reaction

Lewis base: $:NH_3$



Lewis acid: Co^{3+}

Coordination complex: Lewis base (electron pair donor) coordinated to a Lewis acid (electron pair acceptor)

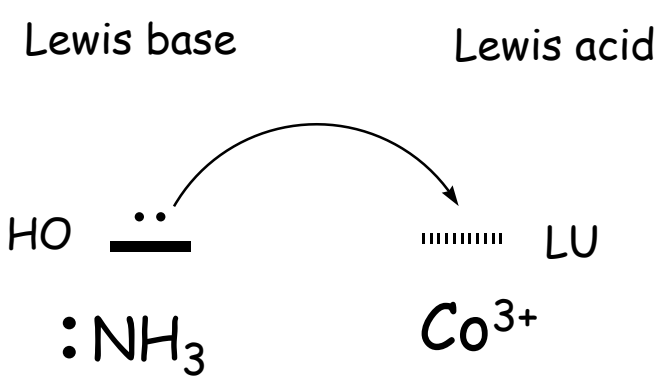
Coordination complex: Ligand (electron donor) coordinated to a metal (electron acceptor)

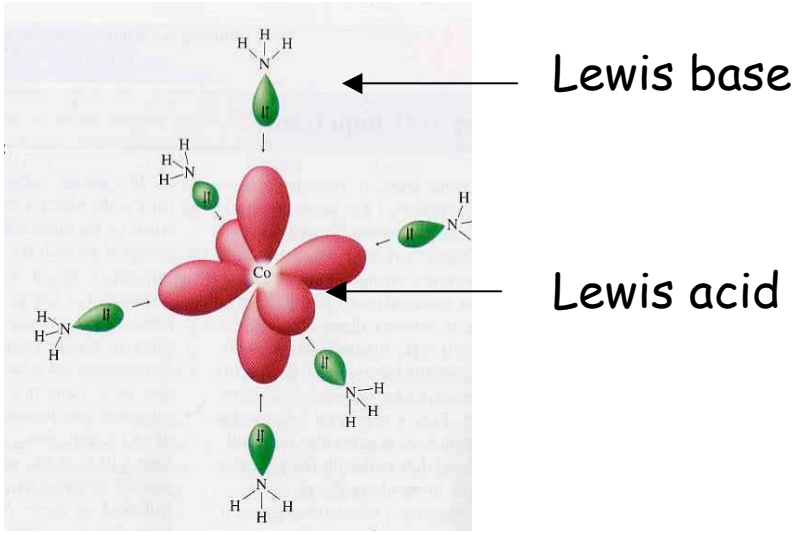
The number of ligand bonds to the central metal atom is termed the coordination number

The basic idea is that the ligand (Lewis base) is providing electron density to the metal (Lewis acid)

The bond from ligand to metal is covalent (shared pair), but both electrons come from the ligand (coordinate covalent bond)

In terms of MO theory we visualize the coordination as the transfer of electrons from the highest occupied valenece orbital (HO) of the Lewis base to the lowest unoccupied orbital (LU) of the Lewis acid





Types of Ligands (electron pair donors: ***Monodentate*** (one tooth) Ligands

Latin: "mono" meaning one and "dens" meaning tooth

TABLE 19–1 Common Monodentate Ligands and Their Names

Ligand	Formula	Name
Fluoride ion	$:F^-$	Fluoro
Chloride ion	$:Cl^-$	Chloro
Nitrite ion	$:NO_2^-$	Nitro
	$:ONO^-$	Nitrito
Carbonate ion	$:OCO_2^{2-}$	Carbonato
Cyanide ion	$:CN^-$	Cyano
Thiocyanate ion	$:SCN^-$	Thiocyanato
	$:NCS^-$	Isothiocyanato
Hydride ion	$:H^-$	Hydrido
Oxide ion	$:O^{2-}$	Oxido
Hydroxide ion	$:OH^-$	Hydroxo
Water	$:OH_2$	Aqua
Ammonia	$:NH_3$	Ammine
Carbon monoxide	:CO	Carbonyl
Nitrogen monoxide	:NO	Nitrosyl

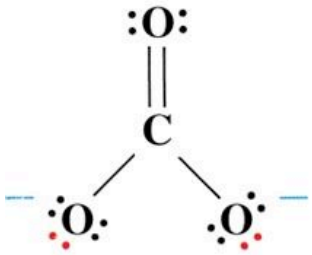
The ligating atom is indicated by a pair of red dots representing a lone pair of electrons. In the CO_3^{2-} ligand, either one or two of the oxygen atoms can donate a lone pair to the metal.

Anions

Molecules with lone pairs

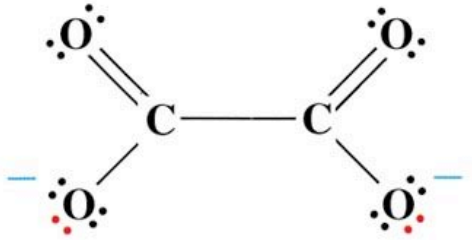
Types of Ligands: Bidentate (two tooth) Ligands

Some common bidentate (chelates):



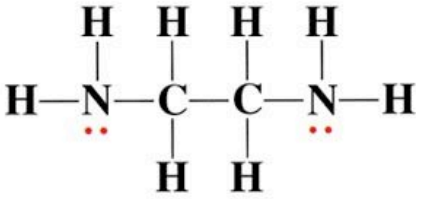
Carbonate ion, CO_3^{2-}

(a)



Oxalate ion, $C_2O_4^{2-}$

(b)

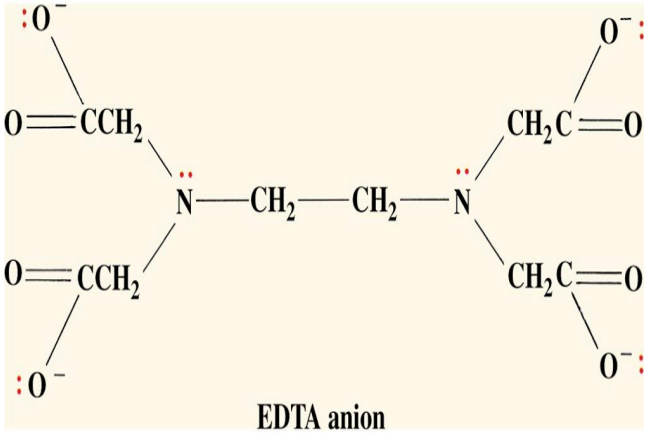


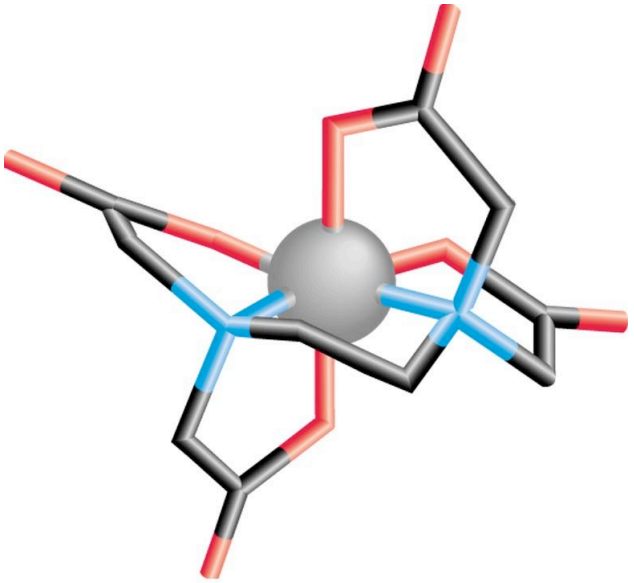
Ethylenediamine, $NH_2\,CH_2\,CH_2\,NH_2$ (en)

(c)

Types of Ligands: Ethylenediaminetetraacetate ion (EDTA): a polydentate *chelating* ligand

Chelate from
Greek *chela*, "claw"





EDTA wraps around the metal ion at all 6 coordination sites producing an exceedingly tight binding to the metal

Alfred Werner
Switzerland
University of Zurich
Zurich, Switzerland
b. 1866
(in Mulhouse, then Germany)
d. 1919

Alfred Werner: the father of the structure of coordination complexes

The Nobel Prize in Chemistry 1913
"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry"

Conventions in writing the structure of coordination compounds:

A coordination compounds is a ***neutral*** species consisting of a coordinate complex and uncoordinated ions that are required to maintain the charge balance

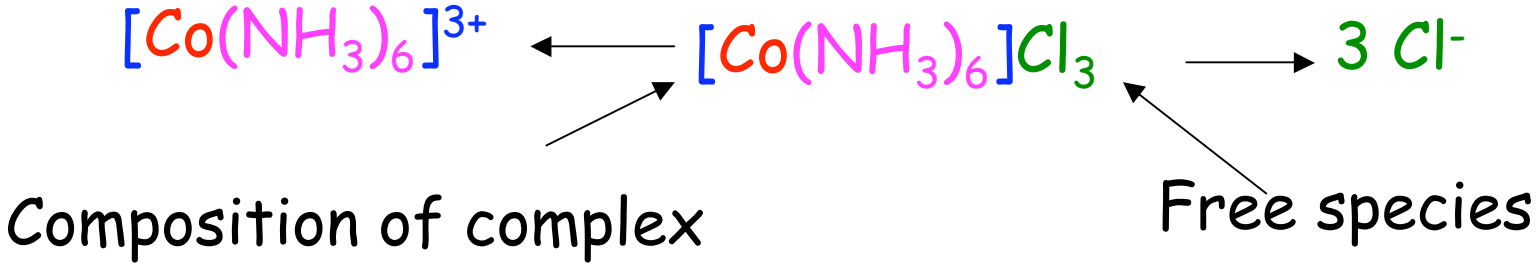
Brackets [] are used to indicate all of the atomic composition of the coordinate complex: the central metal atom and the ligands. The symbol for the central metal atom of the complex is first within the brackets

Species outside of the [] are not coordinated to the metal but are require to maintain a charge balance

(1) A coordination compounds is a ***neutral*** species consisting of a coordinate complex and uncoordinated ions required to maintain the charge balance

(2) Brackets [] are used to indicate all of the atomic composition of the coordinate complex: the central metal atom and the ligands. The symbol for the central metal atom of the complex is first within the brackets

(3) Species outside of the [] are not coordinated to the metal but are require to maintain a charge balance



Ligand substitution reactions

For some complex ions, the coordinated ligands may be substituted for other ligands

Complexes that undergo very rapid substitution of one ligand for another are termed *labile*

Complexes that undergo very slow substitution of one ligand for another are termed *inert*

$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6\ H_2O$ (aqueous)

Werner's explanation of coordination complexes

Metal ions exhibit two kinds of valence: primary and secondary valences

The primary valence is the oxidation number (positive charge) of the metal (usually 2+ or 3+)

The secondary valence is the number of atoms that are directly bonded (coordinated) to the metal

The secondary valence is also termed the "coordination number" of the metal in a coordination complex

Exemplar of primary and secondary valence: $[Co(NH_3)_6]Cl_3$

What is the atomic composition of the complex?	$[Co(NH_3)_6]Cl_3$
What is the net charge of the complex?	$[Co(NH_3)_6]^{3+}$
How do we know the charge is 3+ on the metal?	3+ is required to balance the three Cl^- ions

The primary valence of $[Co(NH_3)_6]Cl_3$ is 3 (charge on Co^{3+})

The secondary valence of $[Co(NH_3)_6]Cl_3$ is 6 (six ligands)

19.2 Structures of Coordination Complexes: The ammonia complexes of Co(III) = Co^{3+}

How did Werner deduce the structure of coordination complexes?

Composition	Ions released	Color
$CoCl_3 \cdot 6NH_3$	3 "free" Cl^- ions	Orange-Yellow
$CoCl_3 \cdot 5NH_3$	2 "free" Cl^- ions	Purple
$CoCl_3 \cdot 4NH_3$	1 "free" Cl^- ions	Green
$CoCl_3 \cdot 3NH_3$	0 "free" Cl^- ions	Green

In all of these complexes there are no free NH_3 molecules
(No reaction with acid)

"free" Cl^- is not in sphere; all NH_3 molecules are is in sphere

Compound 1: $CoCl_3 \cdot 6NH_3 = [Co(NH_3)_6]^{3+}(Cl^-)_3 = [Co(NH_3)_6](Cl)_3$

Conclude: 3 free Cl^- ions, ***complex = $[Co(NH_3)_6]^{3+}$***

Compound 2: $CoCl_3 \cdot 5NH_3 = [Co(NH_3)_5Cl]^{2+}(Cl^-)_2 = [Co(NH_3)_5Cl](Cl)_2$

Conclude: 2 free Cl^- ions, ***complex = $[Co(NH_3)_5Cl]^{2+}$***

Compound 3: $CoCl_3 \cdot 4NH_3 = [Co(NH_3)_4Cl_2]^{1+}(Cl^-) = [Co(NH_3)_4Cl_2](Cl)$

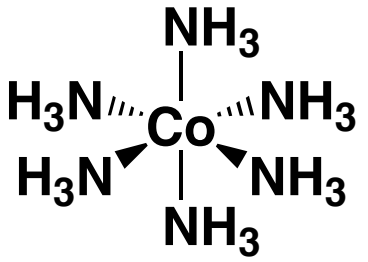
Conclude: 1 free Cl^- ion, ***complex = $[Co(NH_3)_4Cl_2]^{1+}$***

Compound 4: $CoCl_3 \cdot 3NH_3$ = ***$[Co(NH_3)_3Cl_3]$ = complex***

No free Cl^- ions, both Cl^- and NH_3 in sphere

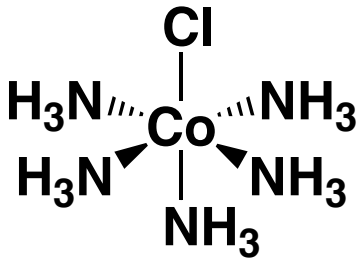
Coordination complexes: Three dimensional structures

$CoCl_3 \cdot 6NH_3$



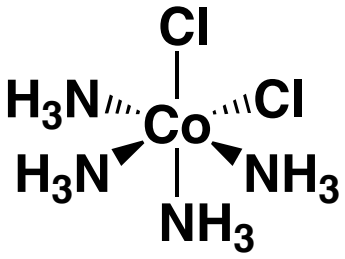
Cl^- Cl^- Cl^-

$CoCl_3 \cdot 5NH_3$

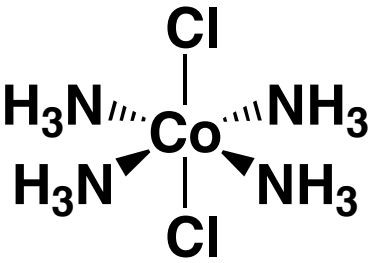


Cl^- Cl^-

$CoCl_3 \cdot 4NH_3$

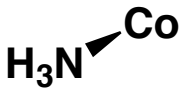


Cl^-



Cl^-

Isomers!

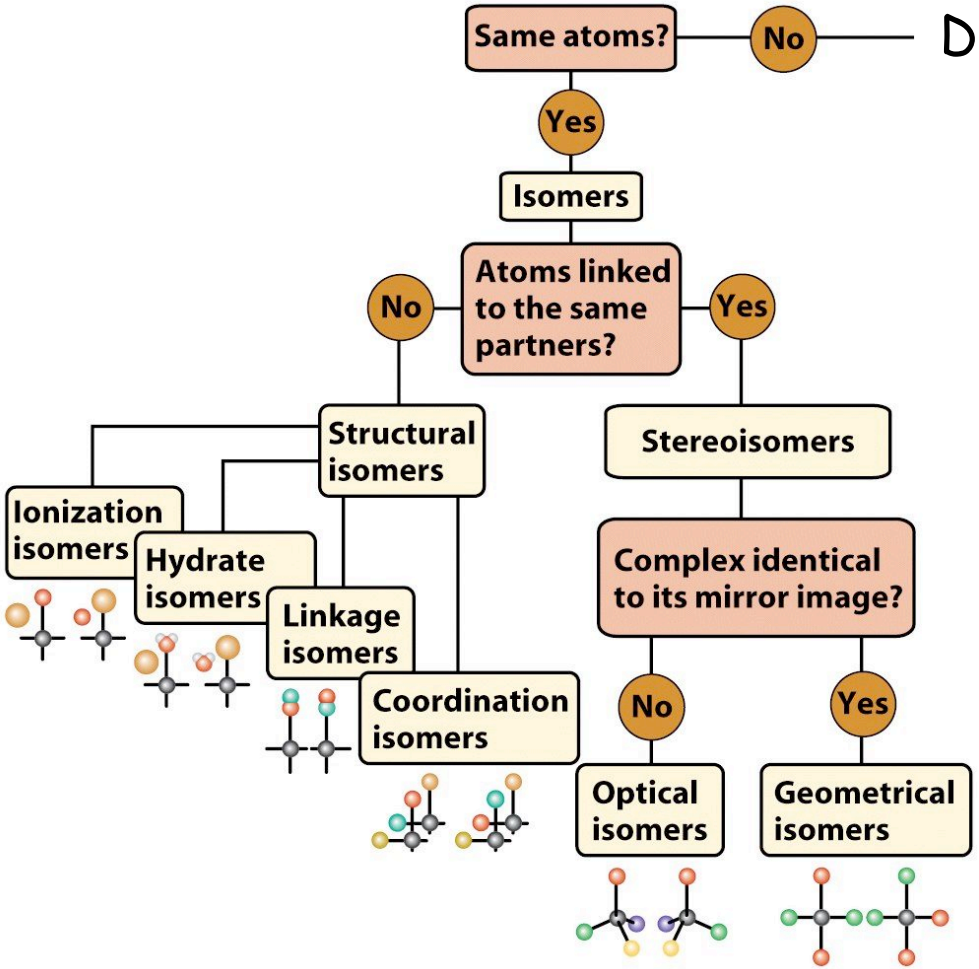


Bond toward you

Bond away from you

Coordination complexes: isomers

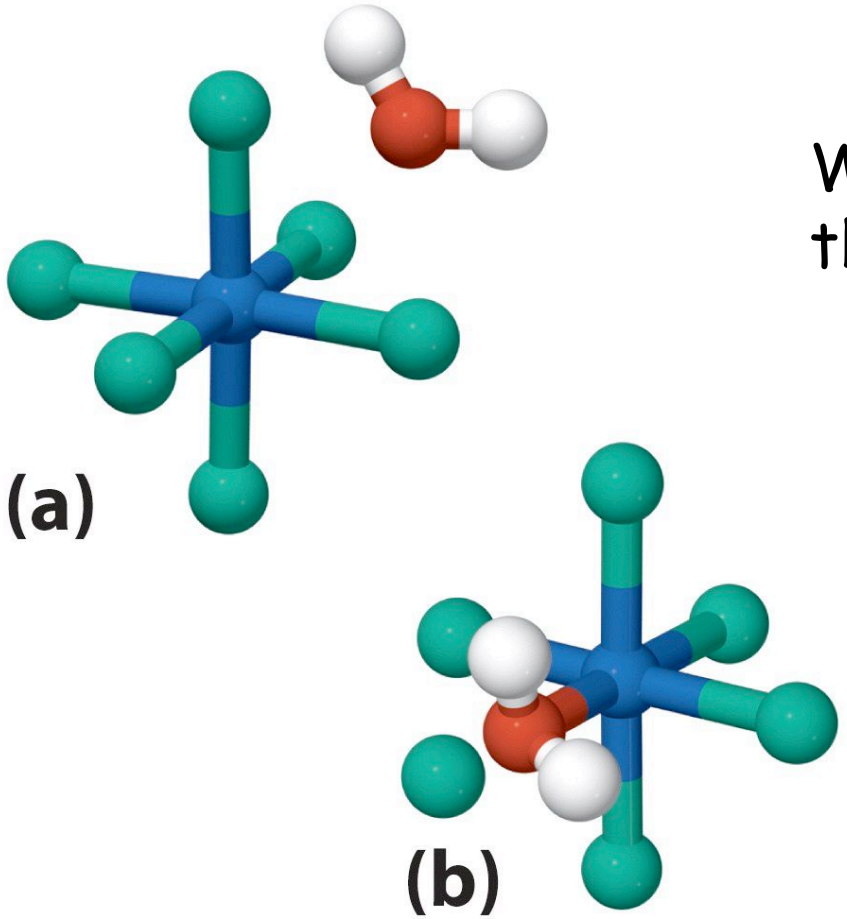
Isomers: same atomic composition, different structures



Different composition!

We'll check out the following types of isomers:
Hydrate
Linkage
Cis-trans
Optical (Enantiomers)

Hydrate isomers:

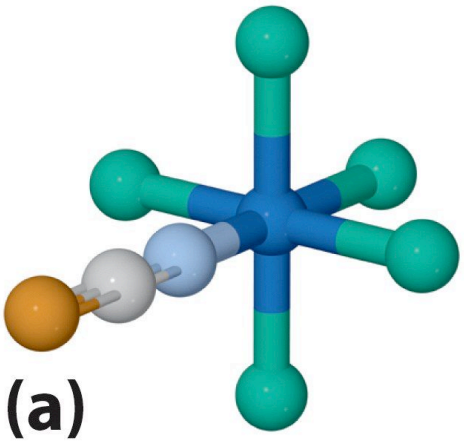


Water in outer sphere (water that is part of solvent)

Water in the inner sphere water (water is a ligand in the coordination sphere of the metal)

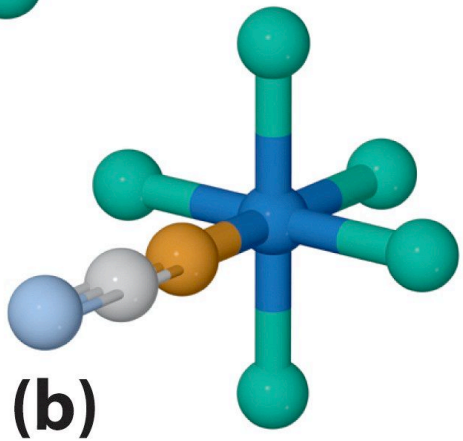
Linkage isomers

Example: $\ominus$S—C≡N Bonding to metal may occur at the S or the N atom



(a)

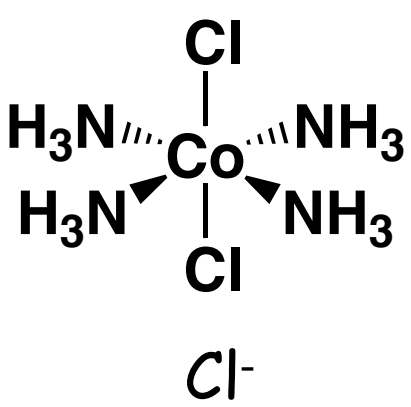
Bonding occurs from N atom to metal

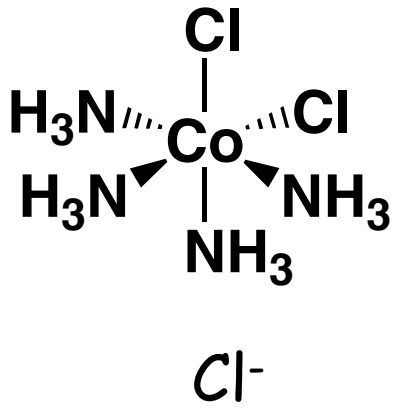


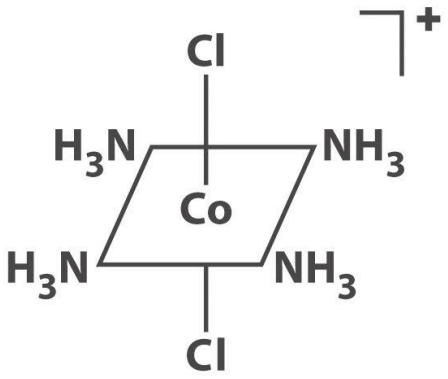
(b)

Bonding occurs from S atom to metal

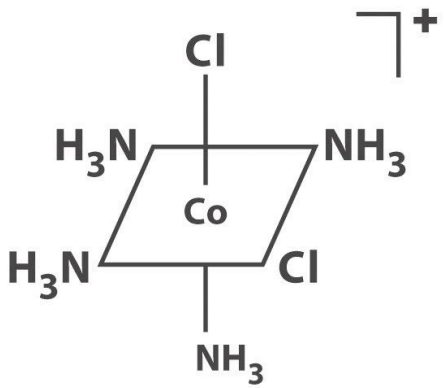
Stereoisomers: geometric isomers (cis and trans)







(a) *trans*-$[CoCl_2(NH_3)_4]^+$



(b) *cis*-$[CoCl_2(NH_3)_4]^+$

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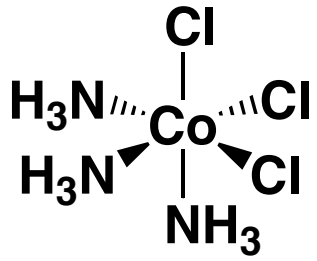
Cis-trans isomers and beyond

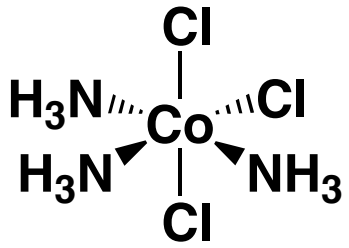
Beyond cis and trans isomers:
facial & meridian isomers and enantiomers

$CoCl_3 \cdot 3NH_3$



facial (fac)

3 NH_3 and 3 Cl ligands are adjacent (on triangular face)



meridian (mer)

3 NH_3 ligands in one plane, 3 Cl ligands in a perpendicular plane

Optical isomers: enantiomers

Mirror images are either superimposible or they are not

Enantiomers are mirror images which are **not** superimposable

Enantiomers do not have a plane of symmetry

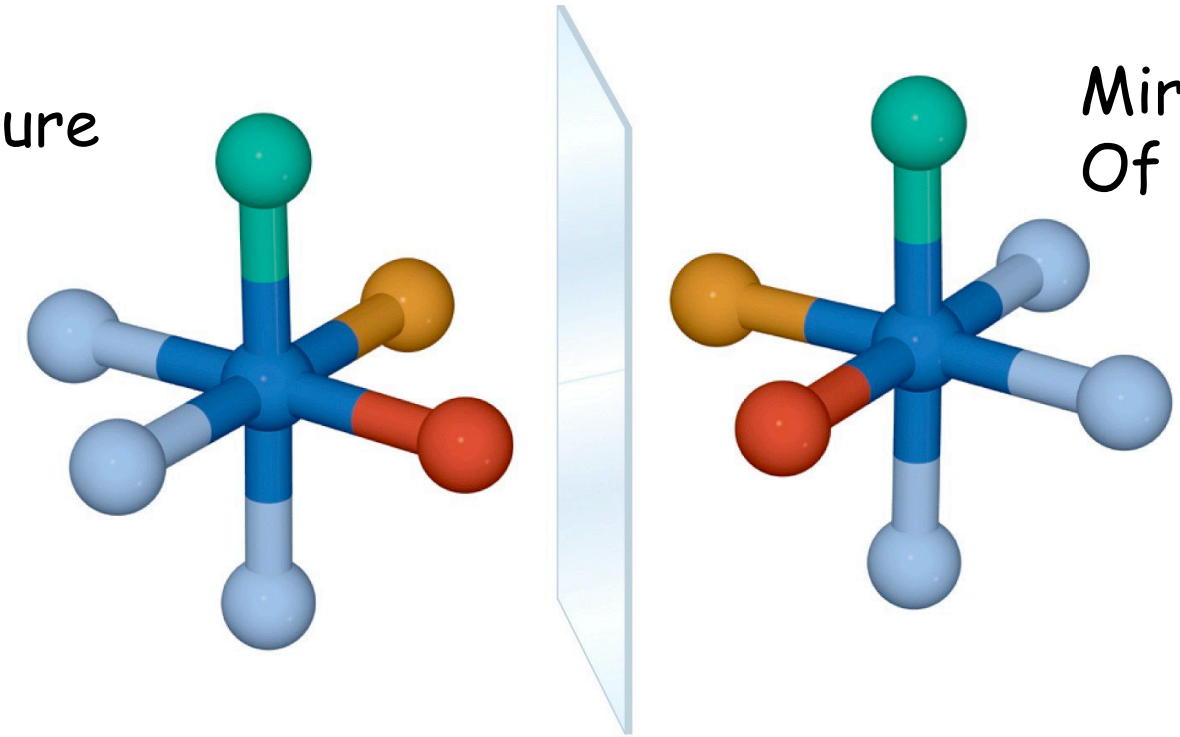
Any molecule which possesses a plane of symmetry is superimposable on its mirror image

Enantiomers rotate polarized light in different directions; therefore, enanotiomers are also termed "optical isomers"

Enantiomers: non superimposable ***mirror images***

A structure is termed ***chiral*** if it is not superimposable on its mirror image

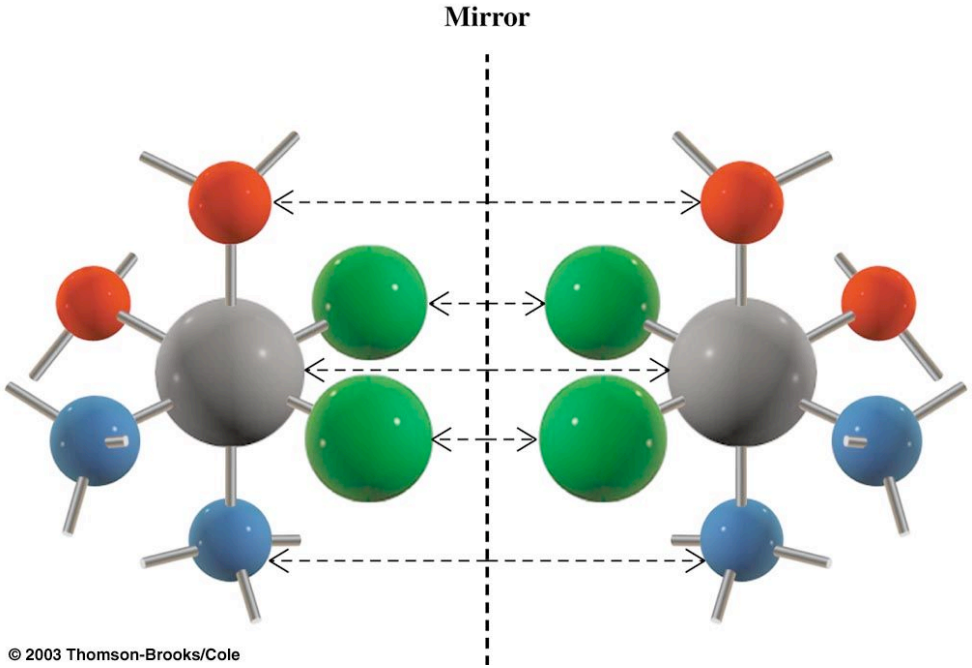
Structure

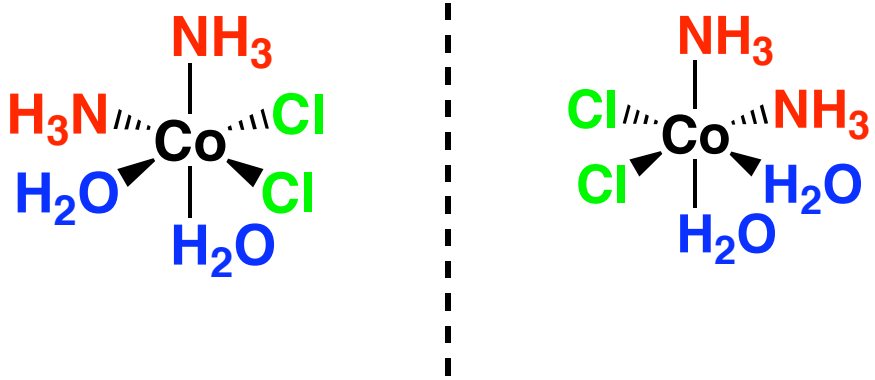


Mirror image
Of structure

Two chiral structures: ***non superimposable mirror images: Enantiomers!***

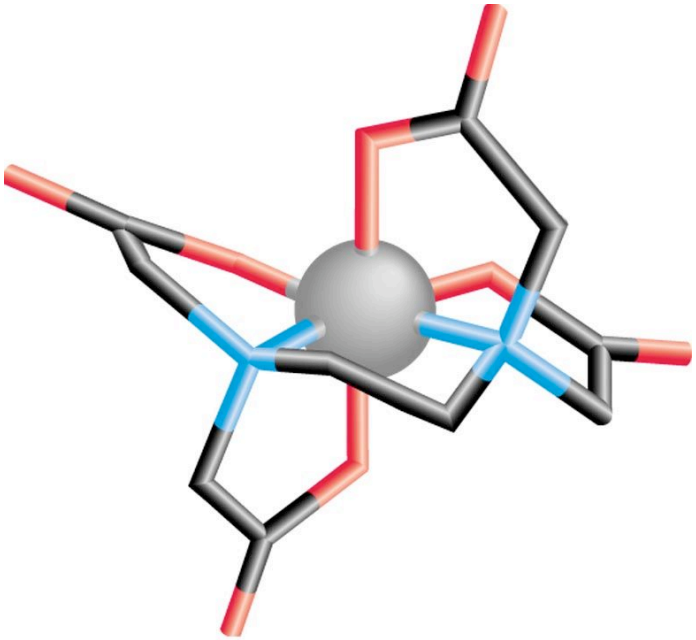
Two coordination complexes which are enantiomers

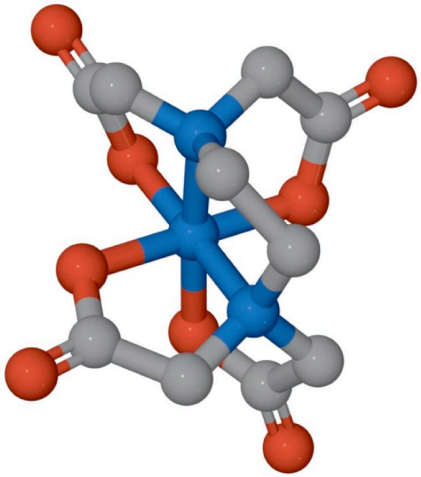




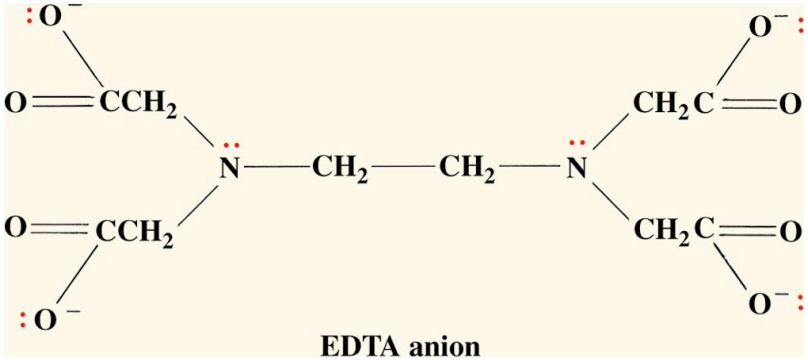
EDTA complexes are optically active

No plane of symmetry





10 An edta complex

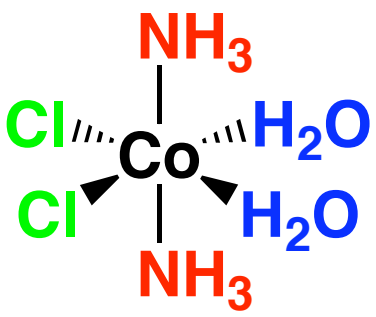


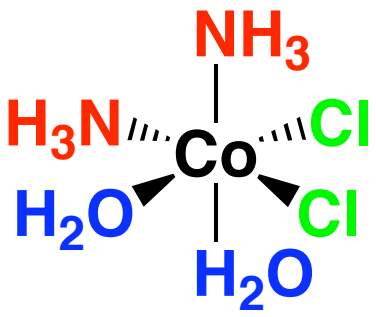
EDTA anion

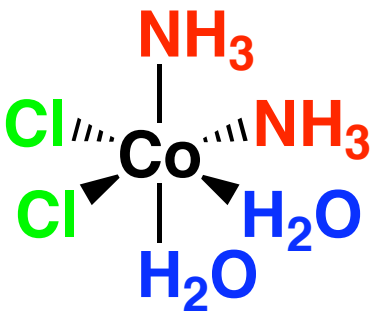
Chirality: the absence of a plane of symmetry
Enantiomers are possible

A molecule possessing a plane of symmetry is achiral and a superimposible 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)?