

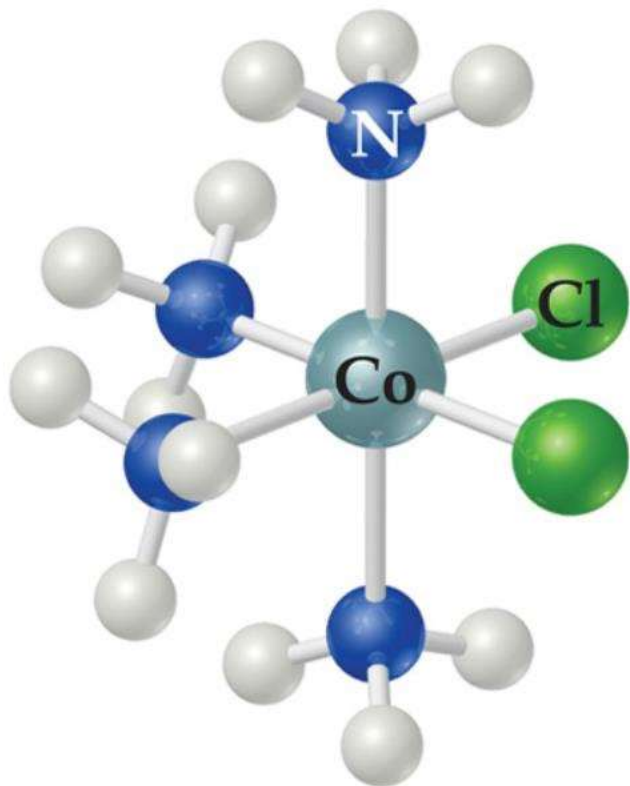
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New Emerging Trends In Co-ordination Chemistry

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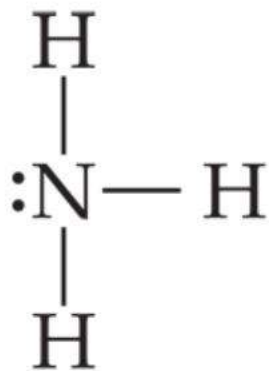
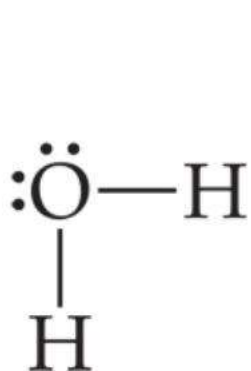
Complexes



- A central metal atom bonded to a group of molecules or ions is a **metal complex**.
- If it's charged, it's a **complex ion**.
- Compounds containing complexes are **coordination compounds**.

Complexes

- The molecules or ions coordinating to the metal are the **ligands**.
- They are usually anions or polar molecules.
- They must have lone pairs to interact with metal



A chemical mystery:

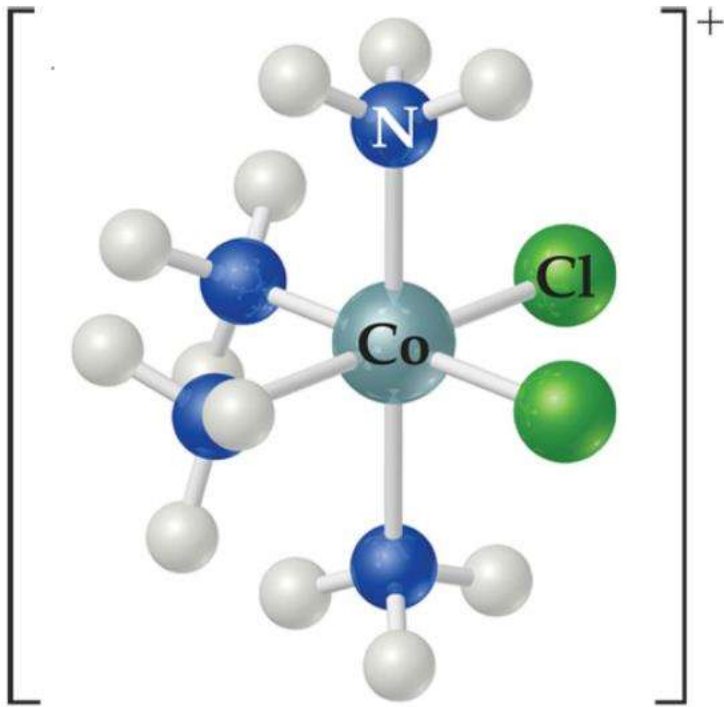
Same metal, same ligands, different number of ions when dissolved

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl ⁻ Ions per Formula Unit	Modern Formulation
CoCl ₃ ·6 NH ₃	Orange	4	3	[Co(NH ₃) ₆]Cl ₃
CoCl ₃ ·5 NH ₃	Purple	3	2	[Co(NH ₃) ₅ Cl]Cl ₂
CoCl ₃ ·4 NH ₃	Green	2	1	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂]Cl
CoCl ₃ ·4 NH ₃	Violet	2	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂]Cl

- Many coordination compounds are brightly colored, but again, same metal, same ligands, different colors.

Werner's Theory



Co(III) oxidation state

Coordination No. is 6

- suggested in 1893 that metal ions have **primary** and **secondary** valences.

- Primary valence equal the metal's oxidation number

- Secondary valency is the number of atoms directly bonded to the metal (coordination number)

Werner's Theory

- The central metal and the ligands directly bonded to it make up the coordination sphere of the complex.
- In $\text{CoCl}_3 \cdot 6\text{NH}_3$, all six of the ligands are NH_3 and the 3 chloride ions are outside the coordination sphere.

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$\text{CoCl}_3 \cdot 6\text{NH}_3$	Orange	4	3	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Purple	3	2	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Green	2	1	<i>trans</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Violet	2	1	<i>cis</i> - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$

Werner's Theory

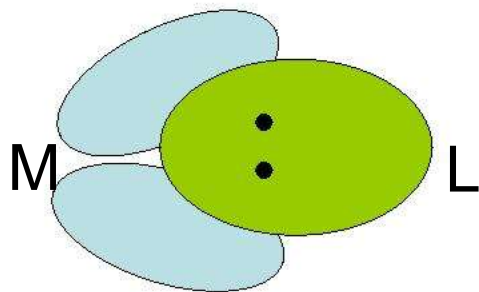
Werner proposed putting all molecules and ions within the sphere in brackets and those “free” anions (that dissociate from the complex ion when dissolved in water) outside the brackets.

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

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CoCl ₃ ·6 NH ₃	Orange	4	3	[Co(NH ₃) ₆]Cl ₃
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CoCl ₃ ·4 NH ₃	Violet	2	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂]Cl

What is Coordination?

- When an orbital from a ligand with lone pairs in it overlaps with an empty orbital from a metal

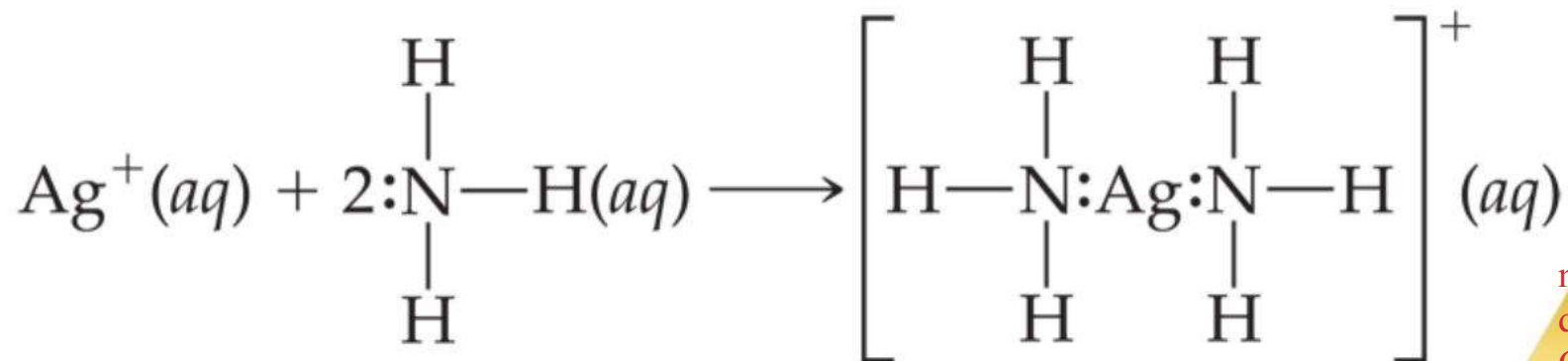


Sometimes called a
coordinate covalent
bond

So ligands *must* have lone pairs of electrons.

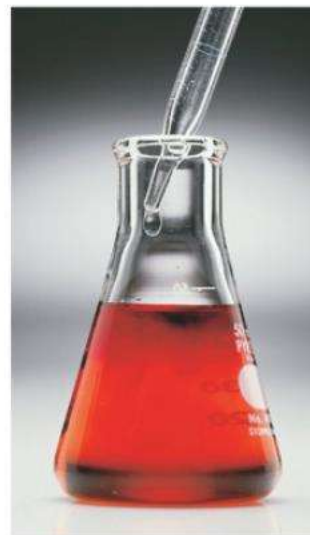
Metal-Ligand Bond

- This bond is formed between a Lewis acid and a Lewis base.
- The ligands (Lewis bases) have nonbonding electrons.
- The metal (Lewis acid) has empty orbitals.

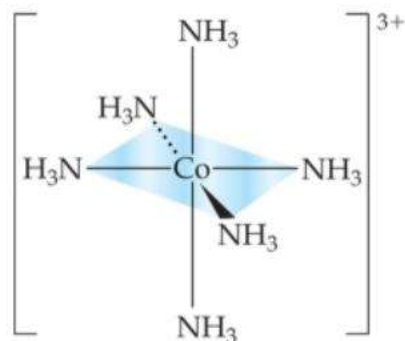
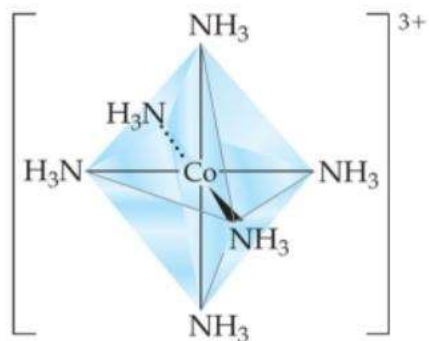
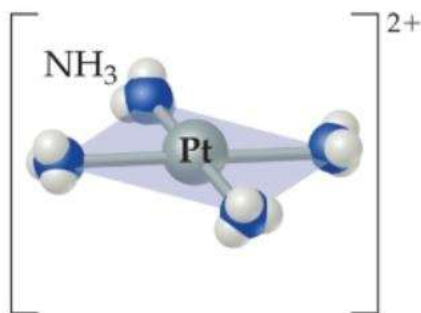
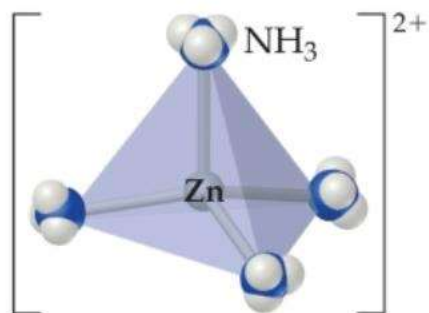


Metal-Ligand Bond

The metal's coordination ligands and geometry can greatly alter its properties, such as color, or ease of oxidation.



Coordination Number

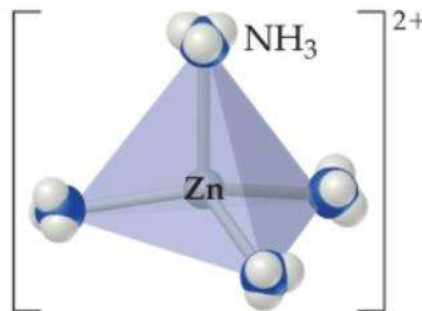


- The atom that supplies the lone pairs of electrons for the metal-ligand bond is the donor atom.
- The number of these atoms is the coordination number.

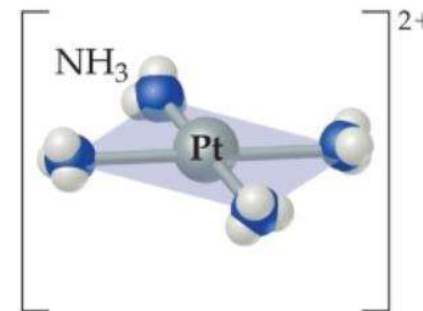
Geometries

- There are two common geometries for metals with a coordination number of four:

- Tetrahedral
- Square planar



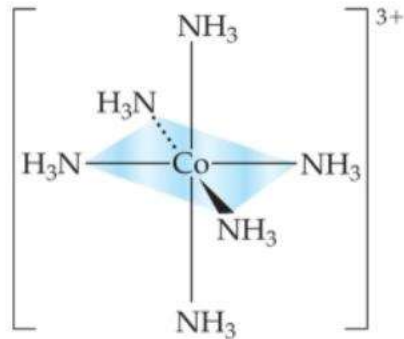
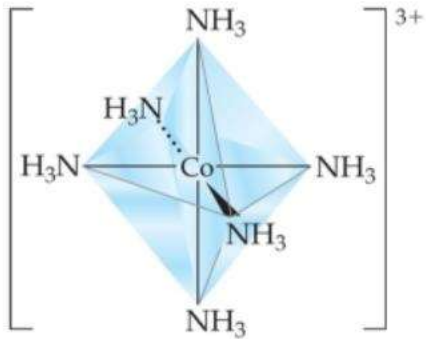
Tetrahedral



Square planar

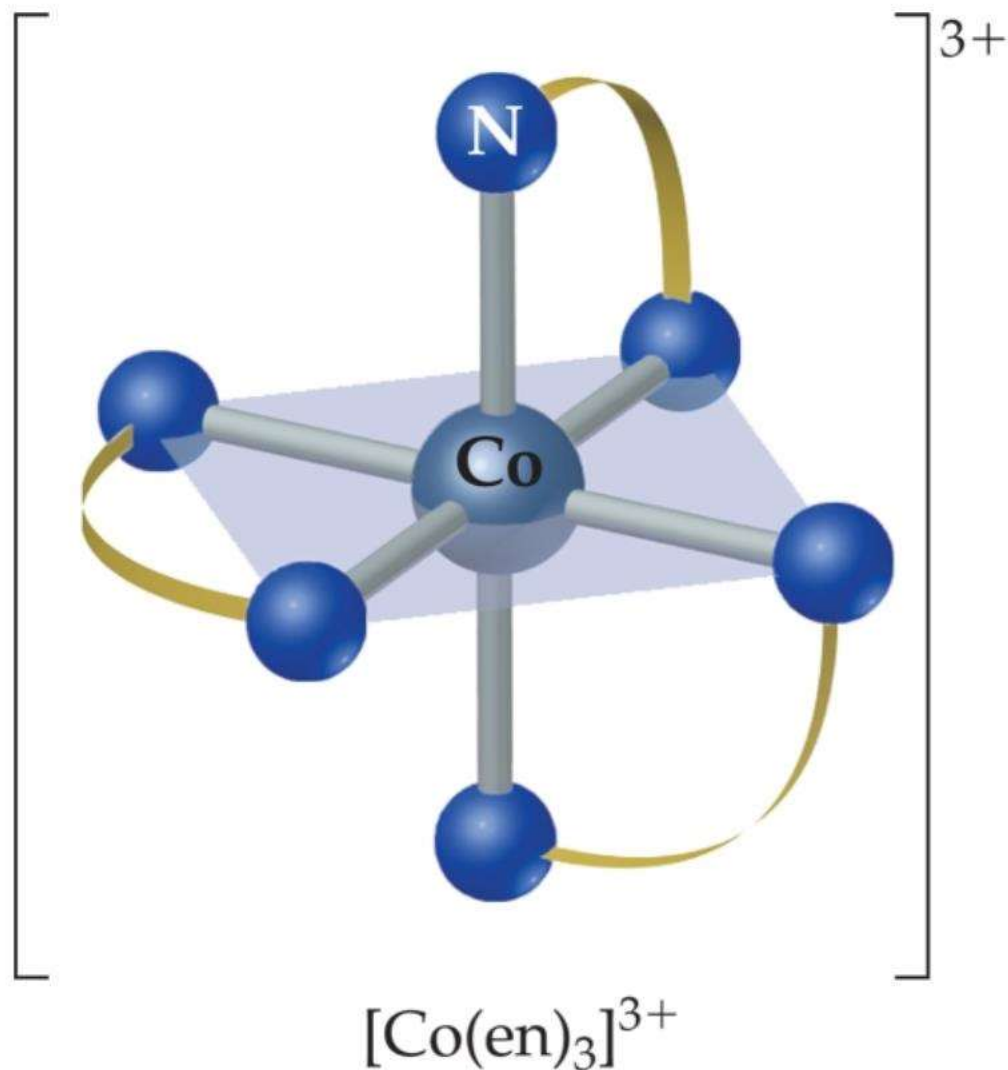
Why square planar? We'll get to that

Geometries



By far the most-encountered geometry, when the coordination number is six, is octahedral.

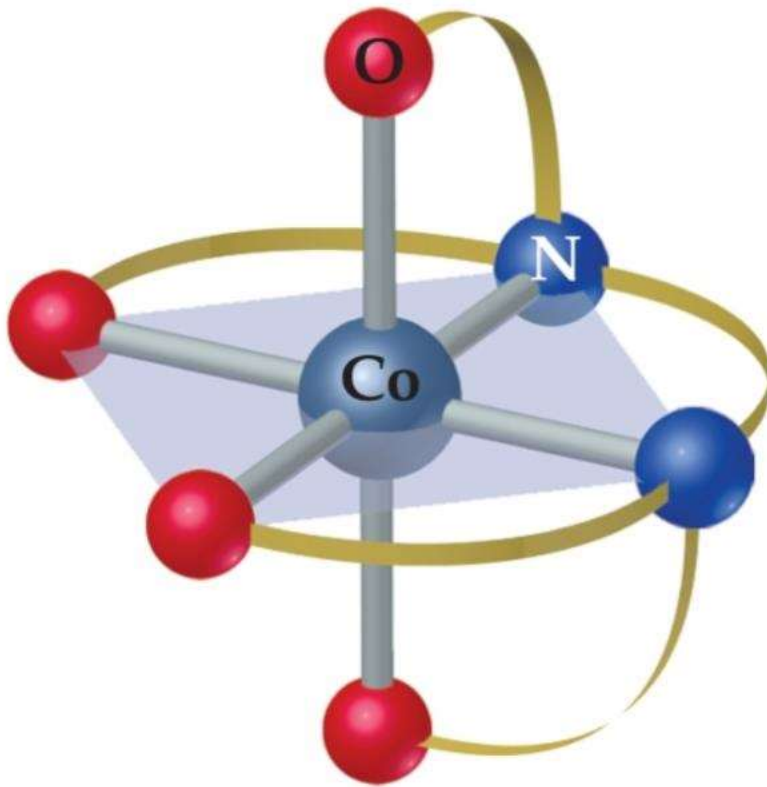
Polydentate Ligands



- Some ligands have two or more donor atoms.
- These are called polydentate ligands or chelating agents.
- In ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ represented here as en, each N is a donor atom.
- Therefore, en is bidentate.

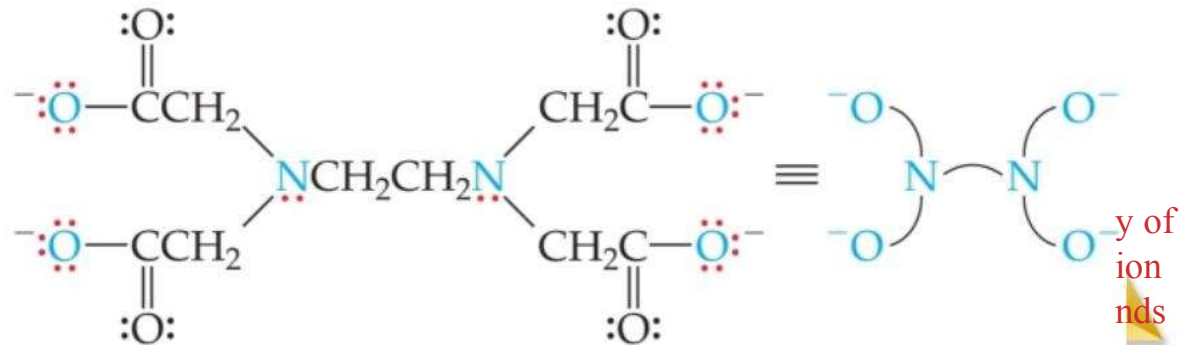
Polydentate Ligands

Ethylenediaminetetraacetate, mercifully abbreviated EDTA, has six donor atoms.



CoEDTA^-

Wraps around the central atom like an octopus



$[\text{EDTA}]^{4-}$

Polydentate Ligands

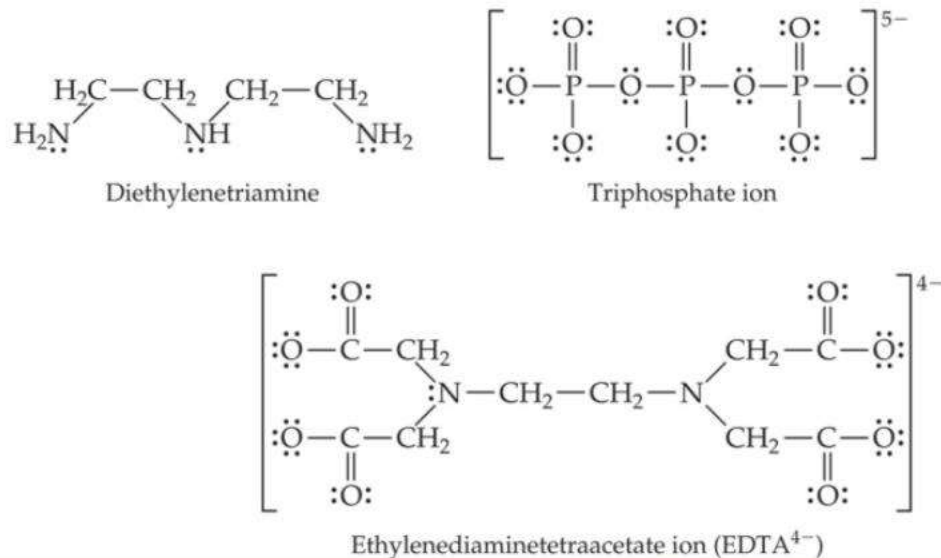
Ligand Type Examples

Monodentate	$\text{H}_2\ddot{\text{O}}:$ Water	$:\ddot{\text{F}}:^-$ Fluoride ion	$[:\text{C}\equiv\text{N}:]^-$ Cyanide ion	$[\ddot{\text{O}}-\text{H}]^-$ Hydroxide ion
	$:\text{NH}_3$ Ammonia	$:\ddot{\text{Cl}}:^-$ Chloride ion	$[\ddot{\text{S}}=\text{C}=\ddot{\text{N}}:]^-$ Thiocyanate ion or	$[\ddot{\text{O}}=\text{N}=\ddot{\text{O}}:]^-$ Nitrite ion or

Bidentate

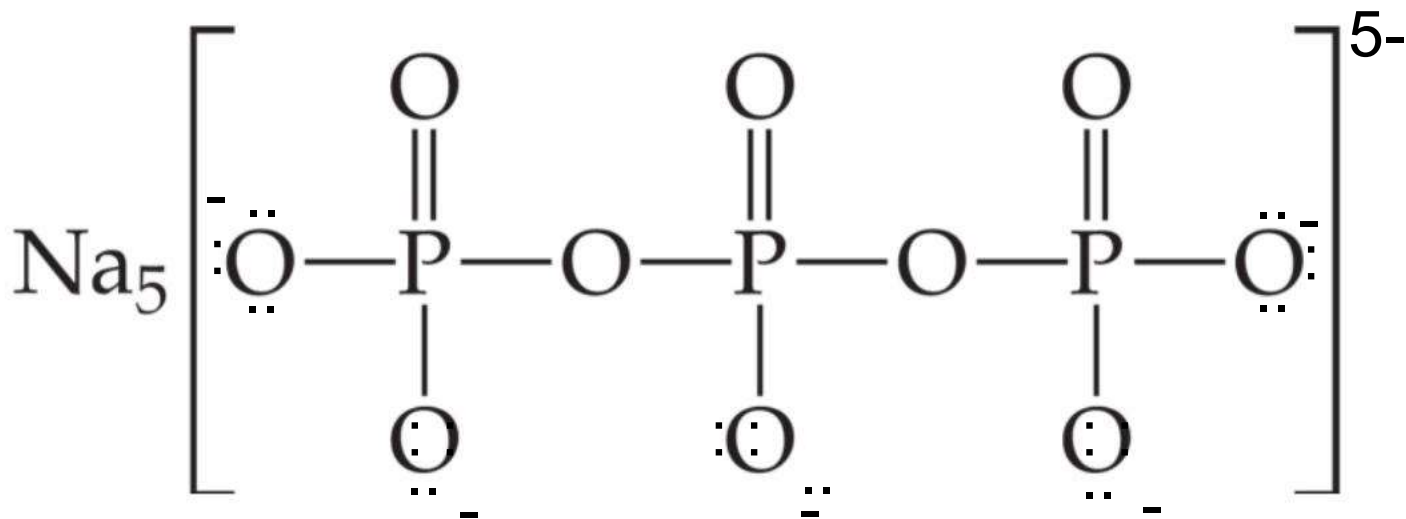


Polydentate



Chelating agents generally form more stable complexes than do monodentate ligands.

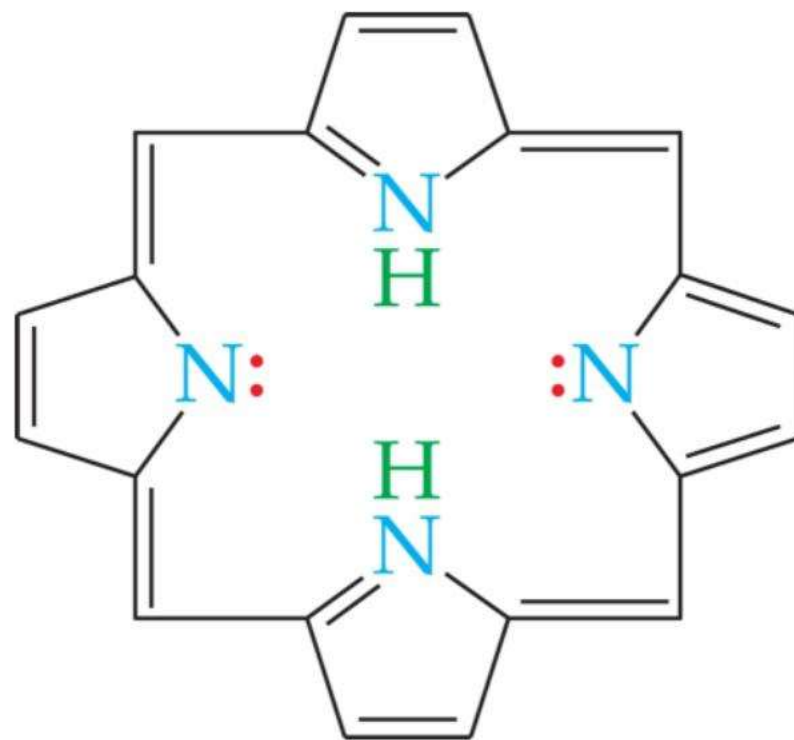
Chelating Agents



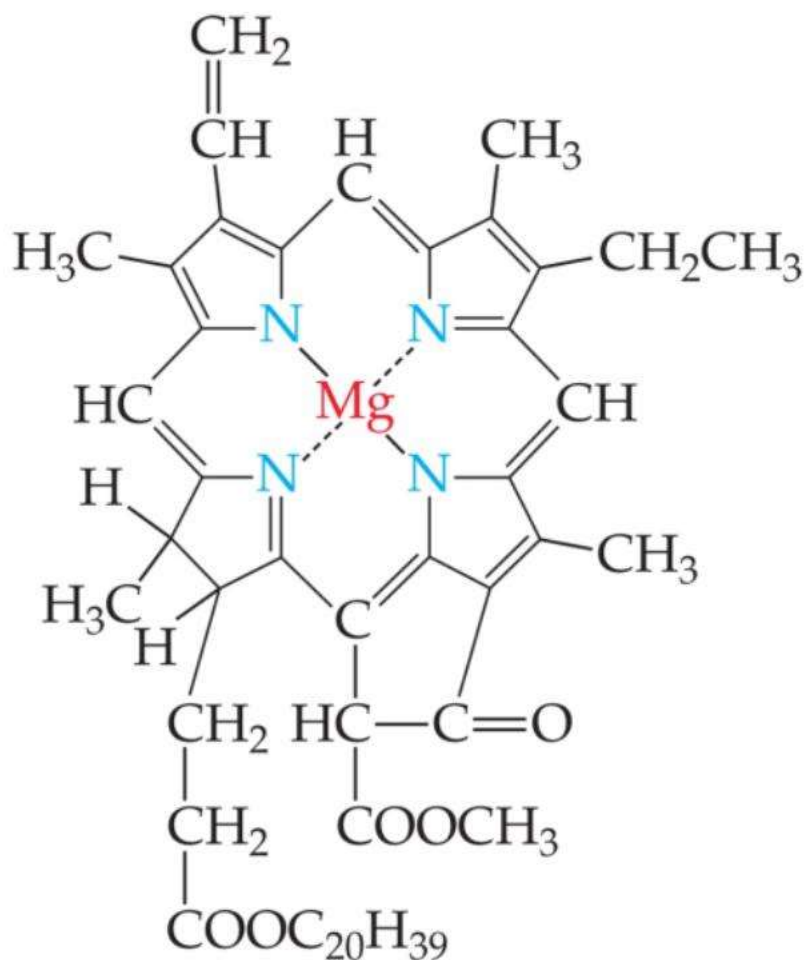
- Bind to metal ions removing them from solution.
- Phosphates are used to tie up Ca^{2+} and Mg^{2+} in hard water to prevent them from interfering with detergents.

Chelating Agents

- Porphyrins are complexes containing a form of the porphine molecule shown at right.
- Important biomolecules like heme and chlorophyll are porphyrins.



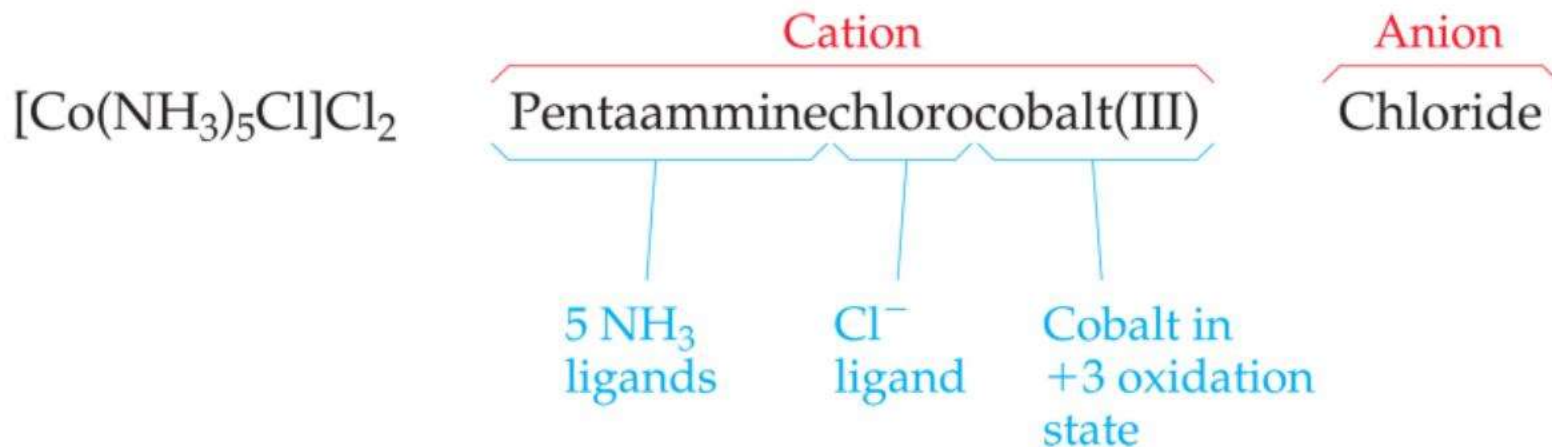
Chelating Agents



Porphines (like chlorophyll *a*) are tetradentate ligands.

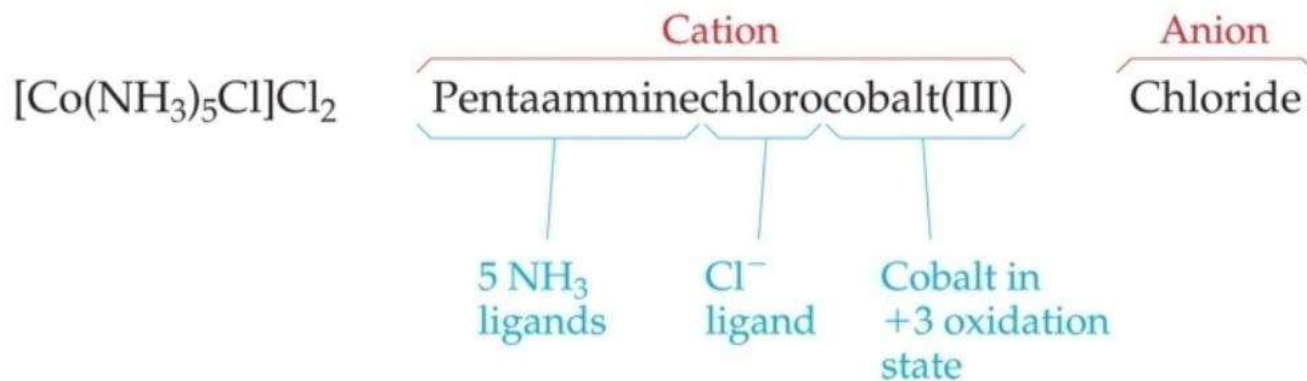
Nomenclature of Co-ordination Compound

- As always the name of the **cation** appears first; the **anion** is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.

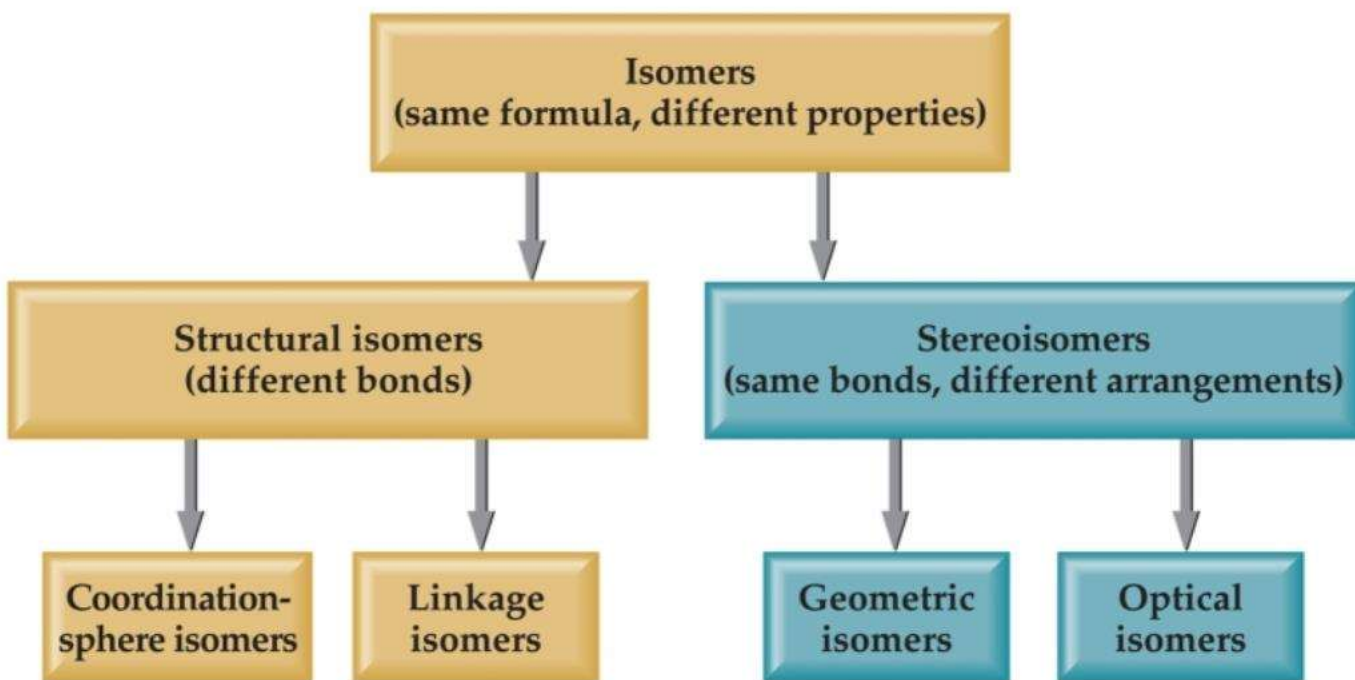


Nomenclature of Co-ordination Compound

- The names of anionic ligands end in “o”; the endings of the names of neutral ligands are not changed.
- Prefixes tell the number of a type of ligand in the complex. If the name of the ligand itself has such a prefix, alternatives like *bis-*, *tris-*, etc., are used.



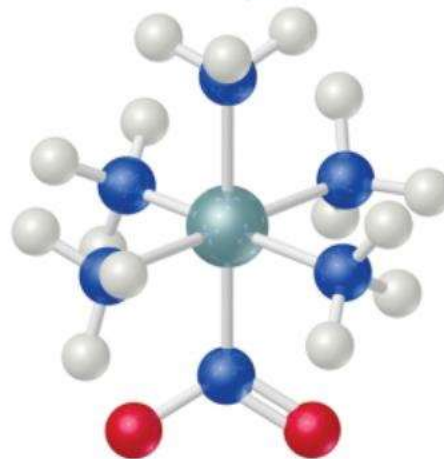
Isomers



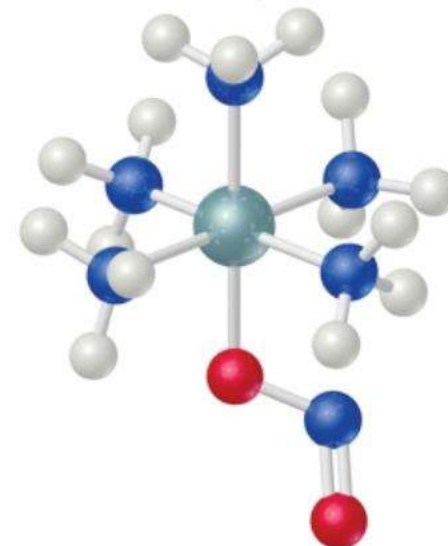
Isomers have the same molecular formula, but their atoms are arranged either in a different order (structural isomers) or spatial arrangement (stereoisomers).

Structural Isomers

If a ligand (like the NO_2 group at the bottom of the complex) can bind to the metal with one or another atom as the donor atom, linkage isomers are formed.

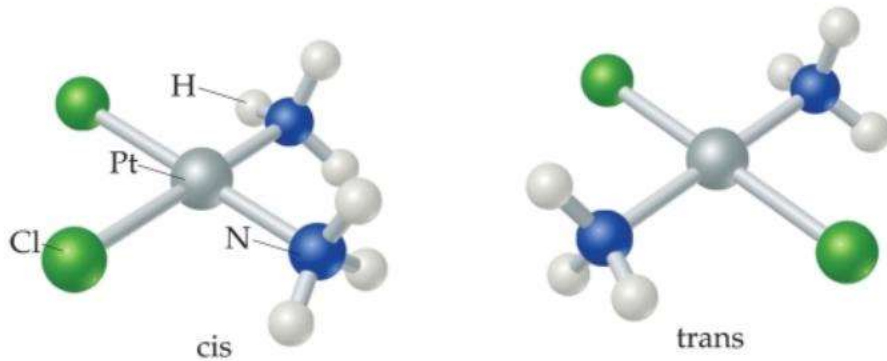


Nitro isomer



Nitrito isomer

Geometric isomers



- With these geometric isomers, two chlorines and two NH₃ groups are bonded to the platinum metal, but are clearly different.

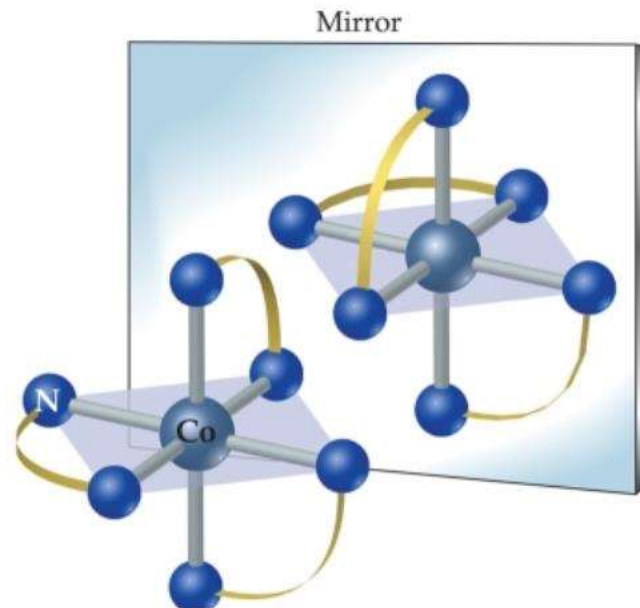
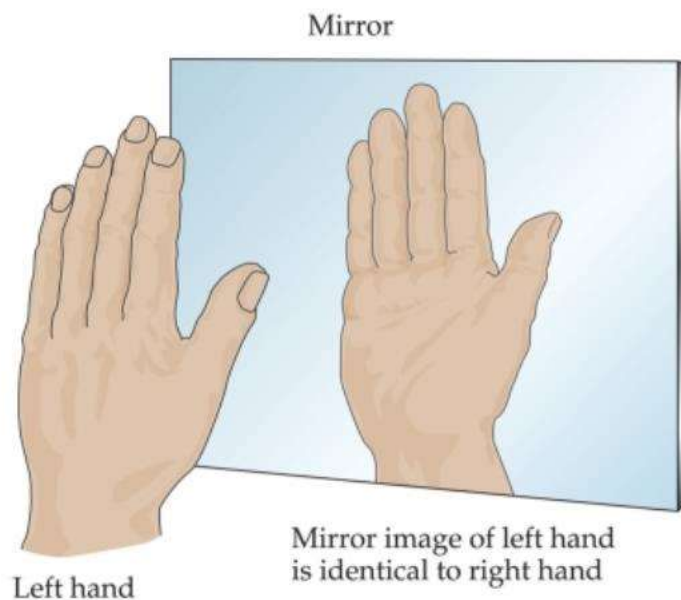
- *cis*-Isomers have like groups on the same side.
- *trans*-Isomers have like groups on opposite sides.

of each atom the same

Bonding the same

Arrangement in space different

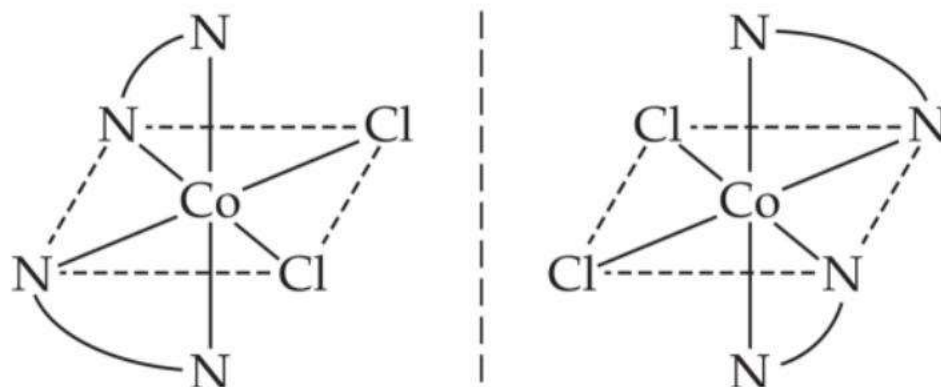
Stereoisomers



- Other stereoisomers, called **optical isomers** or **enantiomers**, are mirror images of each other.
- Just as a right hand will not fit into a left glove, two enantiomers cannot be superimposed on each other.

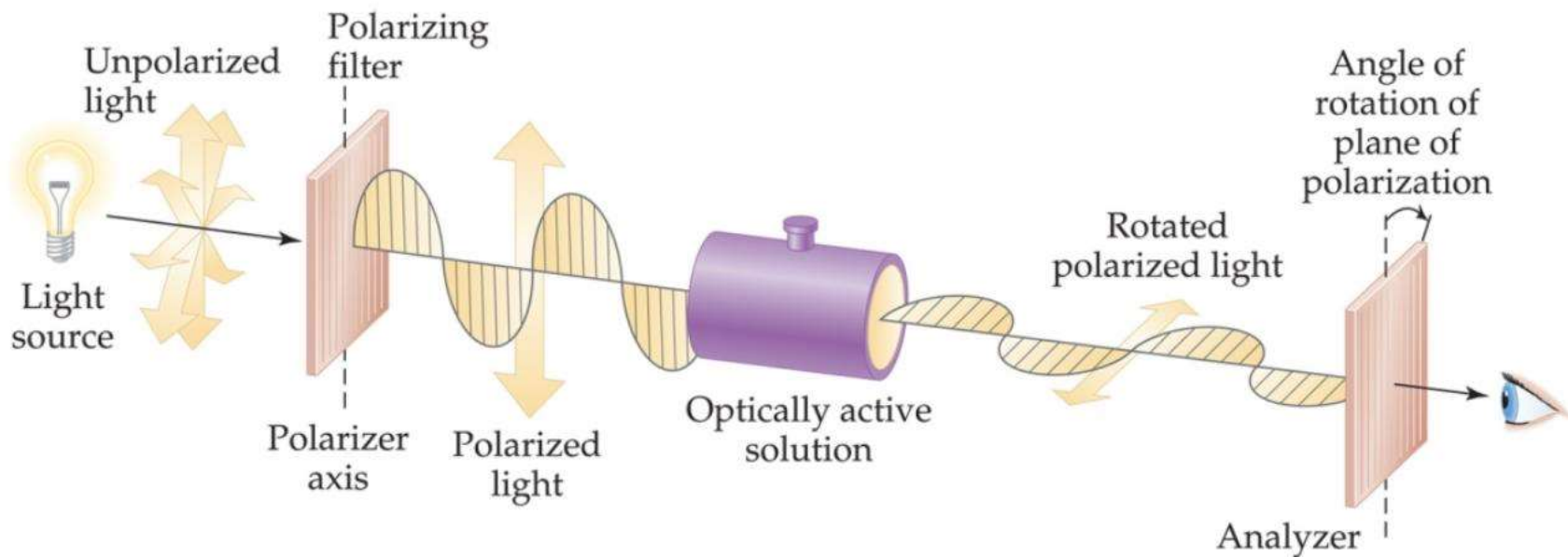
Enantiomers

A molecule or ion that exists as a pair of enantiomers is said to be **chiral**.



Enantiomers

- Most of the physical properties of chiral molecules are the same, boiling point, freezing point, density, etc.
- One exception is the interaction of a chiral molecule with plane-polarized light.



Explaining the properties of transition metal coordination complexes

1. Magnetism

2. color

Metal complexes and color

The ligands of a metal complex effect its color

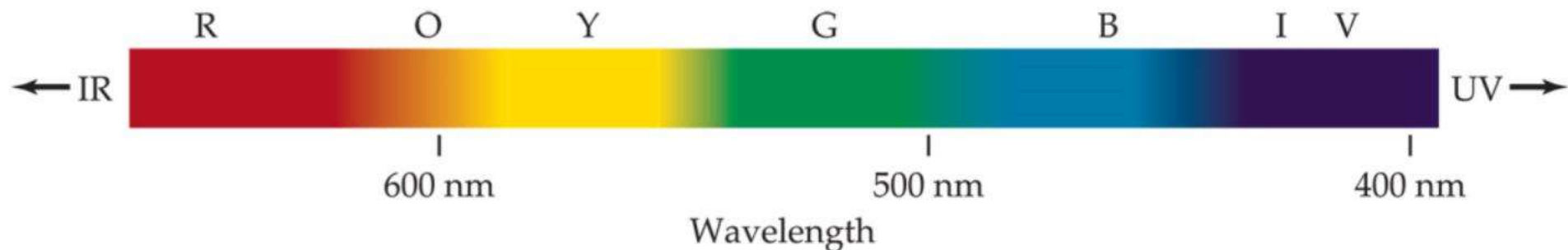


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Addition of NH_3 ligand to $\text{Cu}(\text{H}_2\text{O})_4$ changes its color



Why does anything have color?



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Light of different frequencies give different colors

We learned that elements can *emit* light of different frequency or color.

But these coordination complexes are not emitting light

They *absorb* light.

How does that give color?

Complimentary color wheel

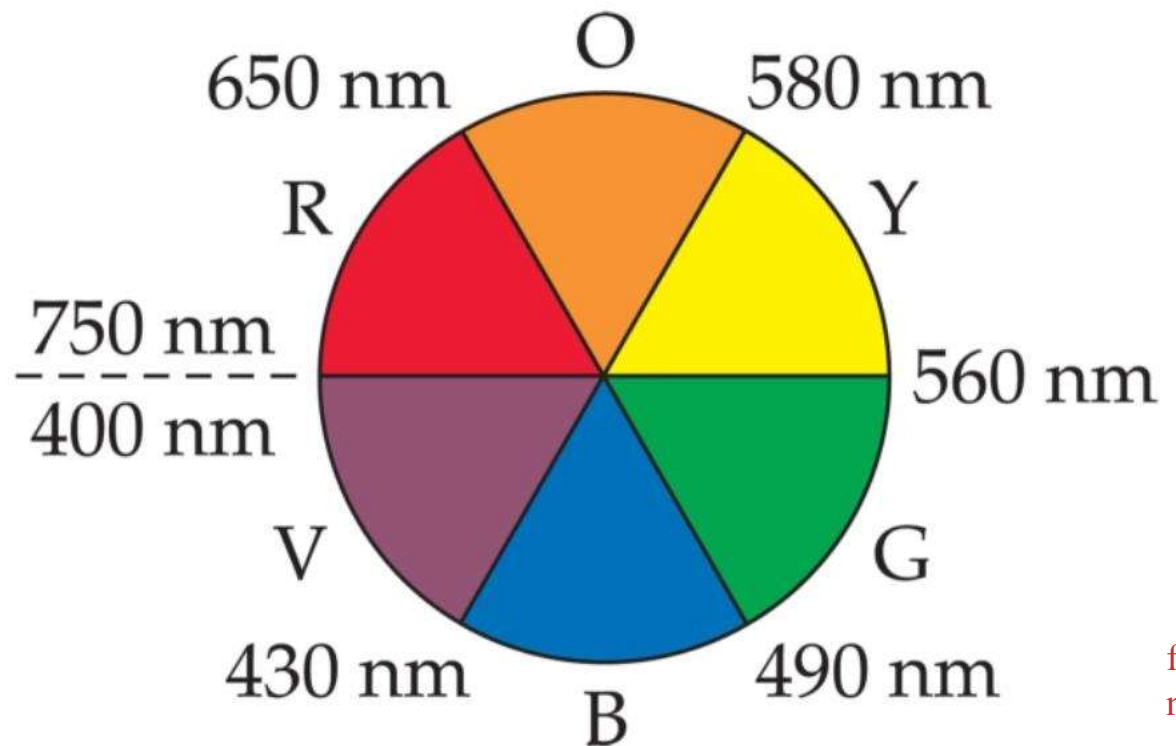
If one color absorbed, the color opposite is perceived.

Absorb **Orange**

See **Blue**

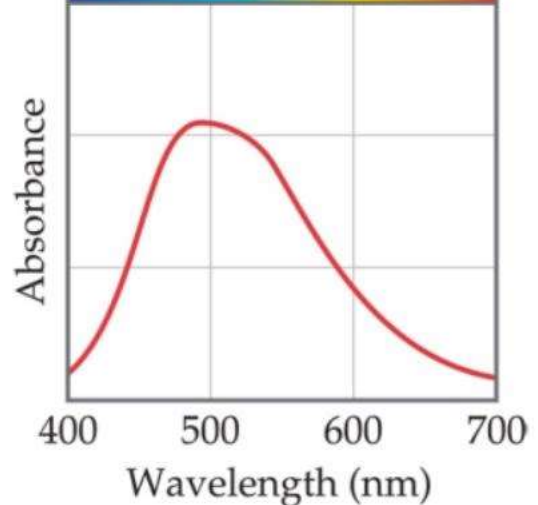
Absorb **Red**

See **Green**

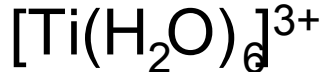




(a)



(b)



Absorbs in green yellow.

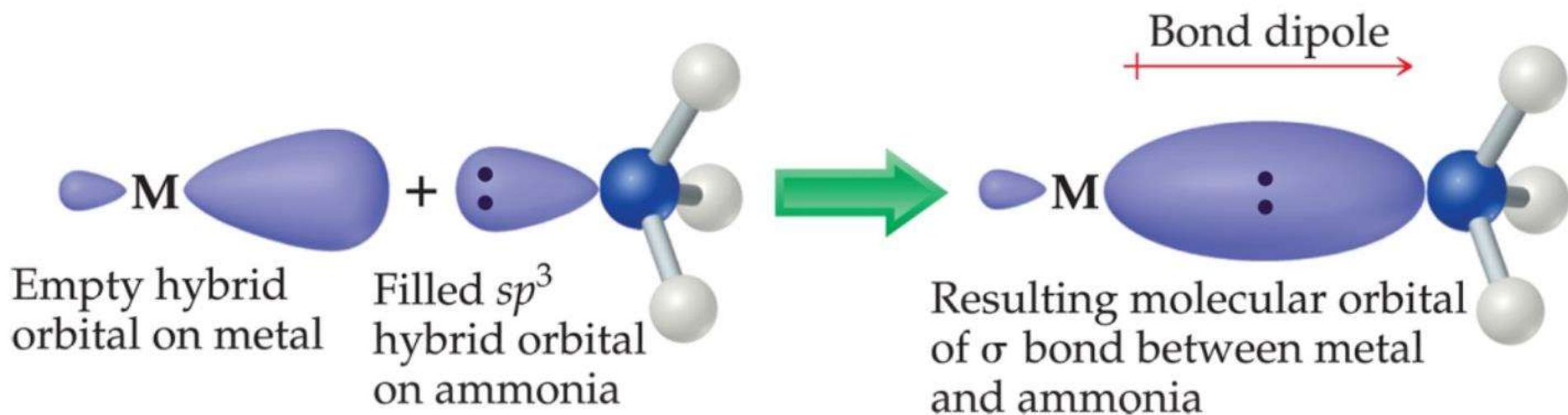
Looks purple.

Model of ligand/metal bonding.

Electron pair comes from ligand

Bond very polarized.

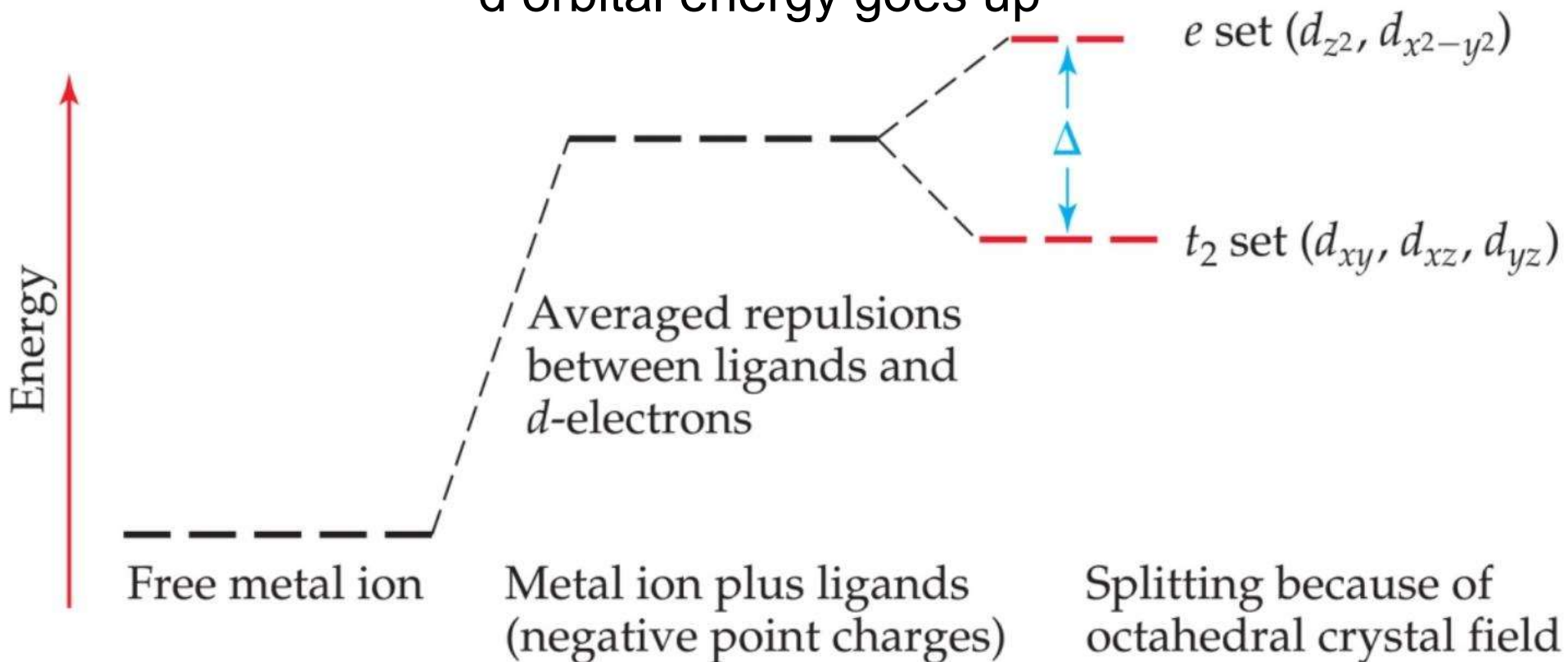
Assumption: interaction pure electrostatic.



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Now, think of point charges being attracted to metal nucleus
Positive charge. What about electrons in d orbitals?

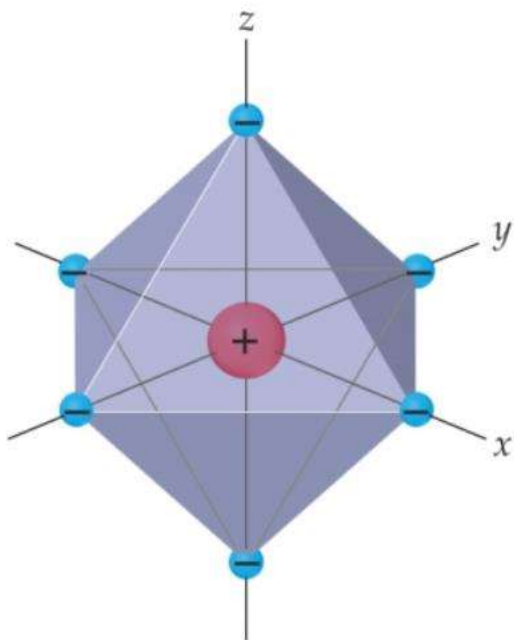
Ligand negative charge
Is repelled by d electrons,
d orbital energy goes up



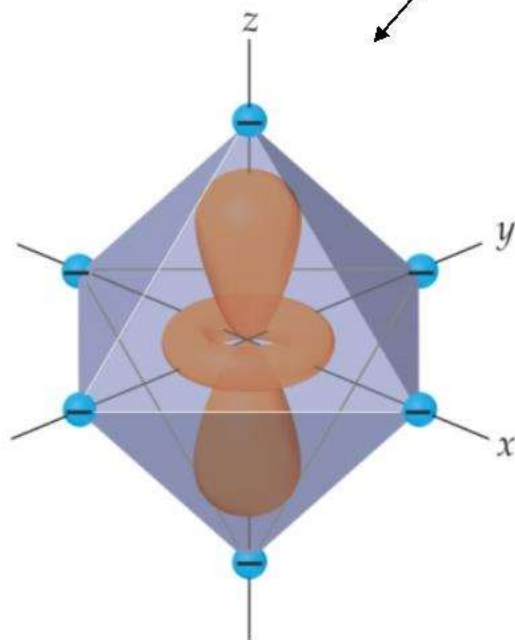
Ligands will interact with some d orbitals more than others

Depends on relative orientation of orbital and ligand

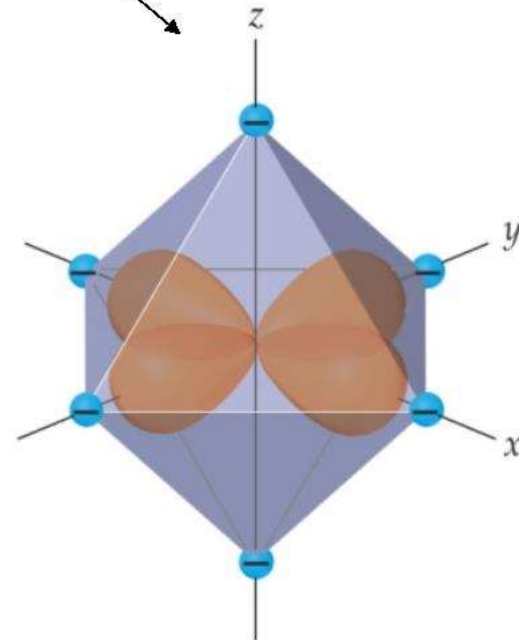
Ligands point right at lobes



(a)

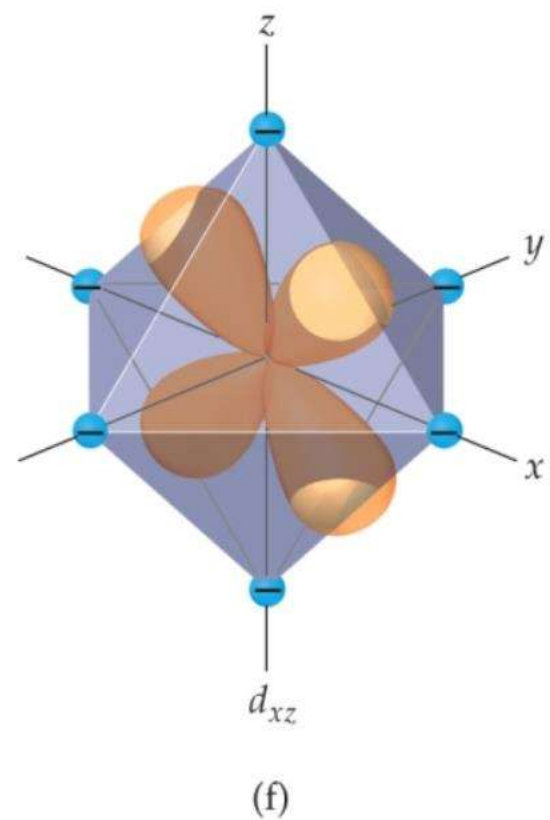
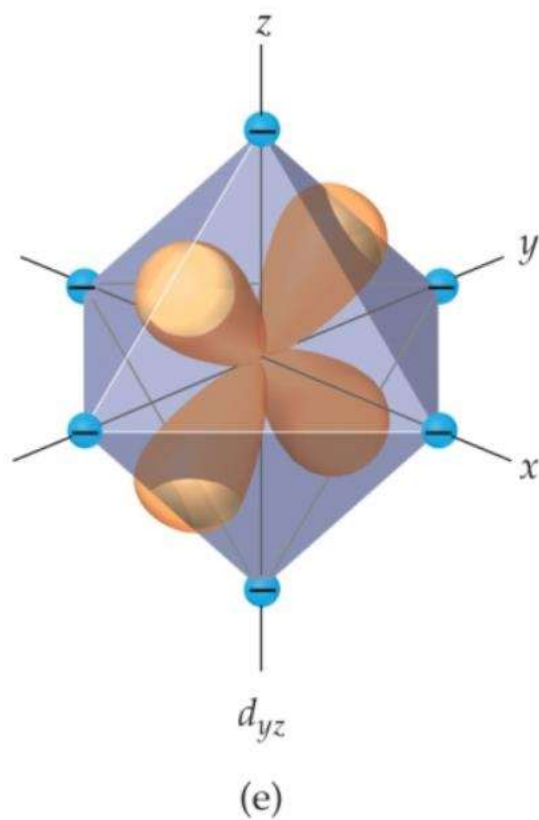
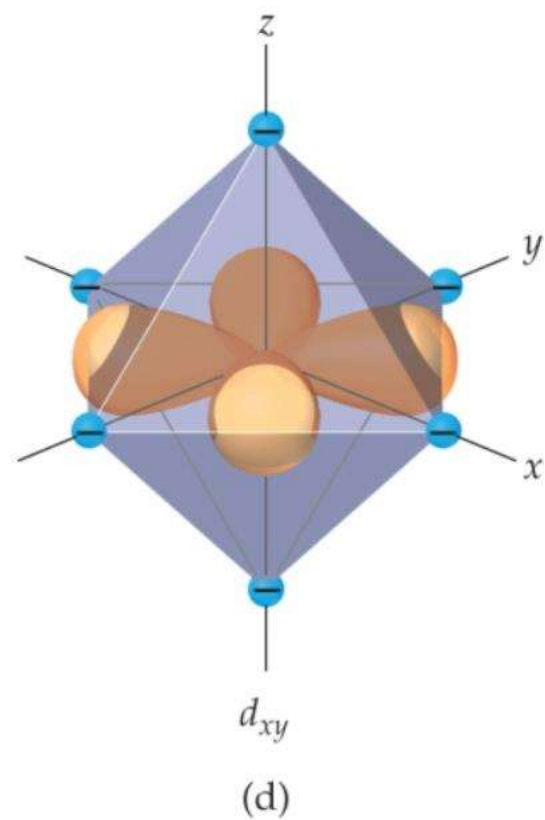


(b)

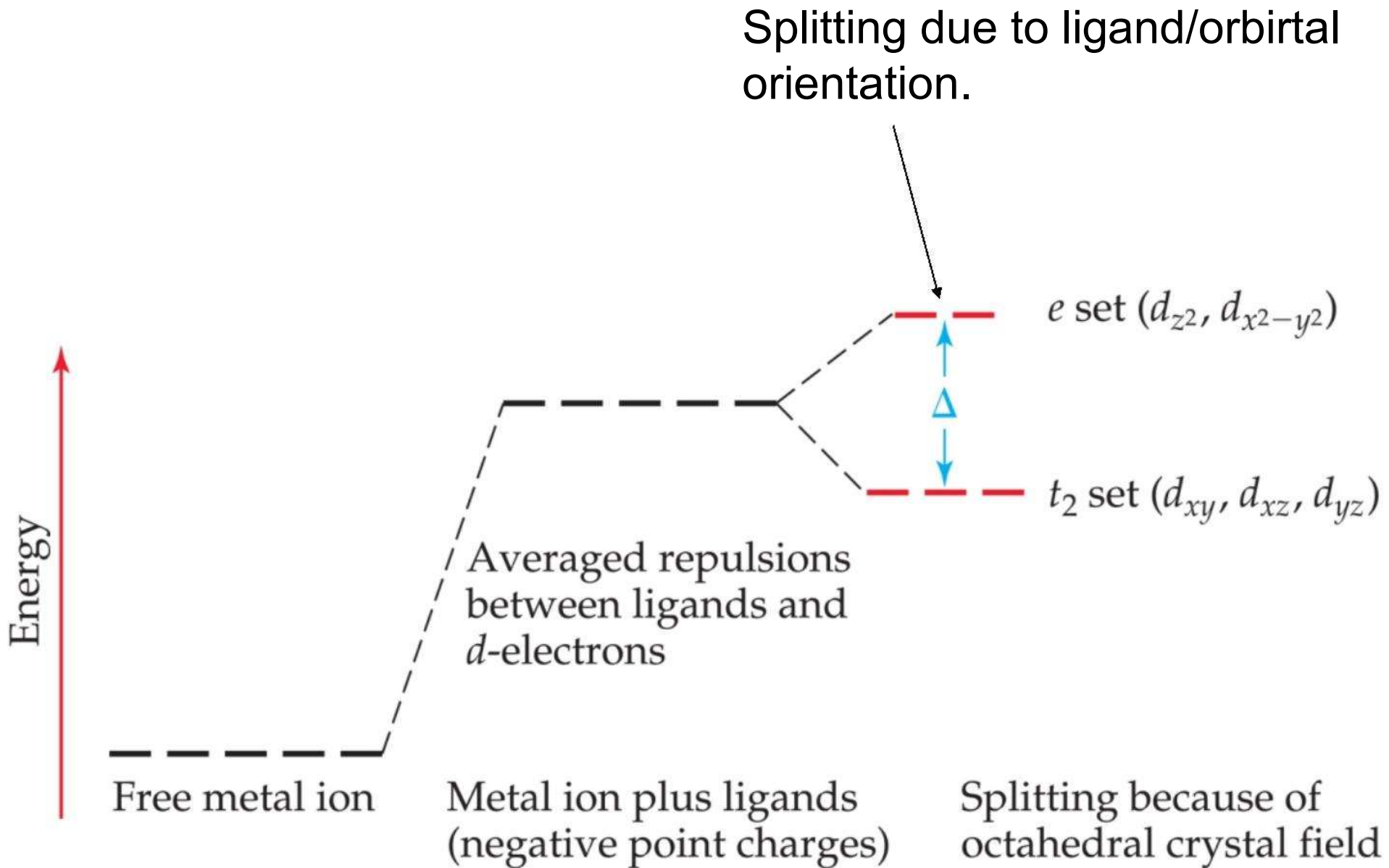


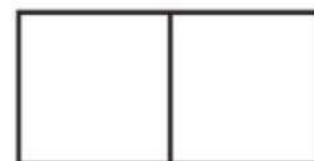
(c)

In these orbitals, the ligands are between the lobes
Interact less strongly



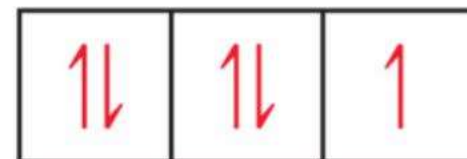
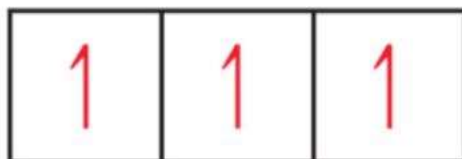
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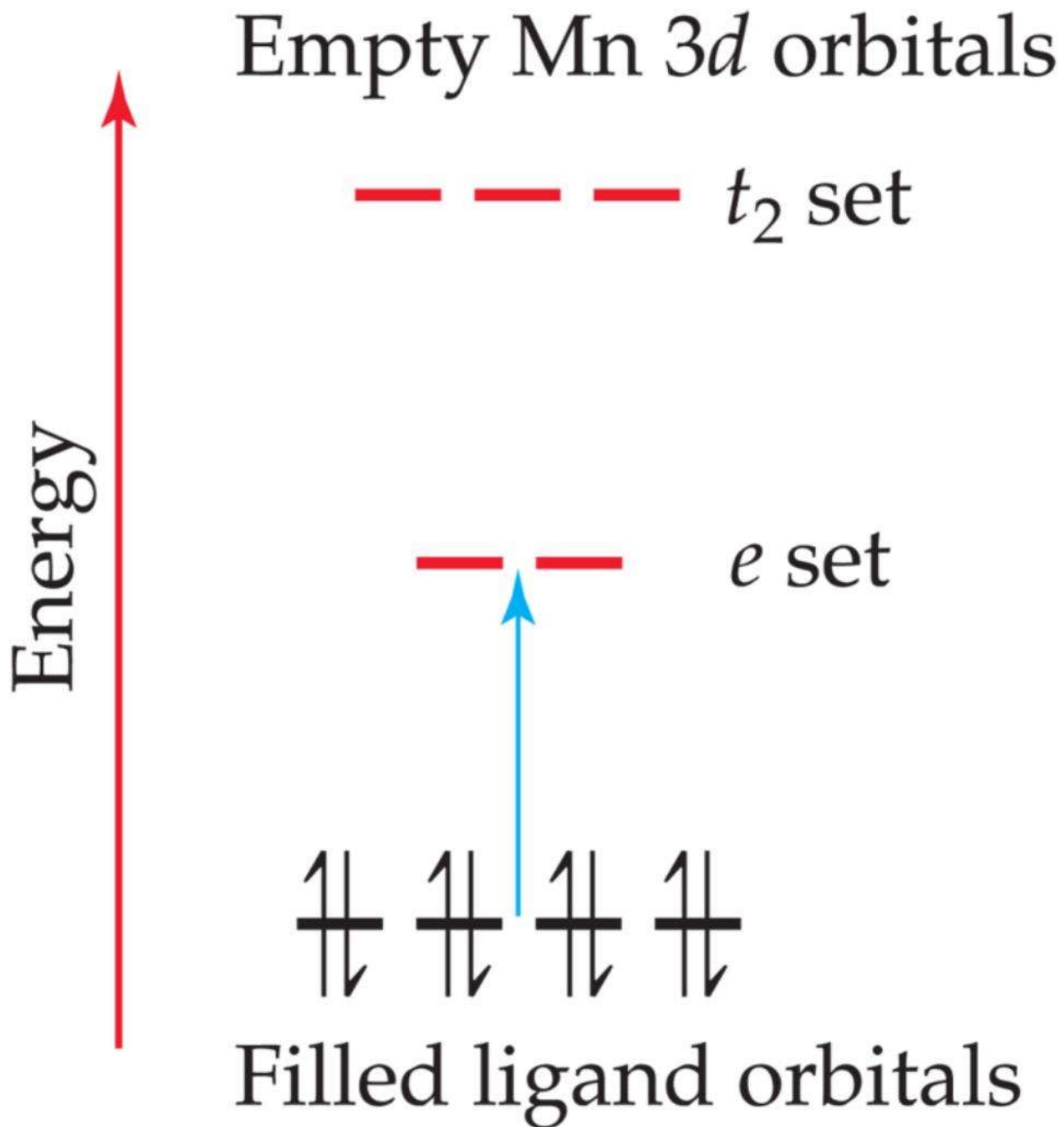


High spin

Low spin



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Explaining the properties of metal complexes

Magnetism and color

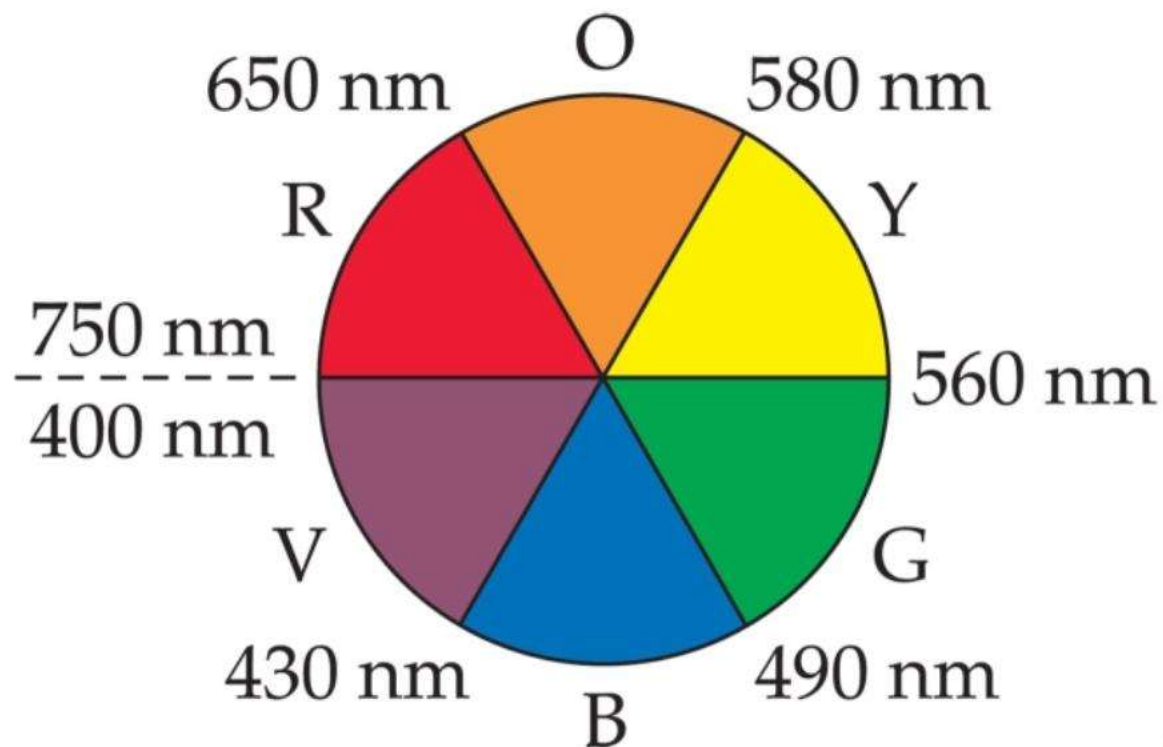
How does seeing color work?

Absorb **Orange**

See **Blue**

Absorb **Red**

See **Green**



Overall Project Goals

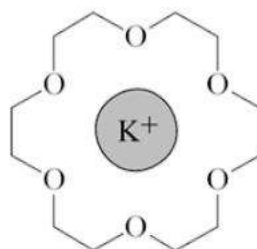
- Design and Synthesize Ligands to stabilize transition metal ions in harsh aqueous conditions
- Synthesize and Characterize transition metal complexes of the ligands (Mn and Fe preferred)
 - Evaluate complexes as oxidation catalysts in pH 10 water with H_2O_2 or O_2 as oxidant
 - Determine mechanism(s) and preferred substrates of active catalysts
- Redesign Ligands for improved activity



Metal-Ligand Binding Affinity

- ***Complementarity***: match between metal and ligand leading to molecular recognition (minimum for strong binding)

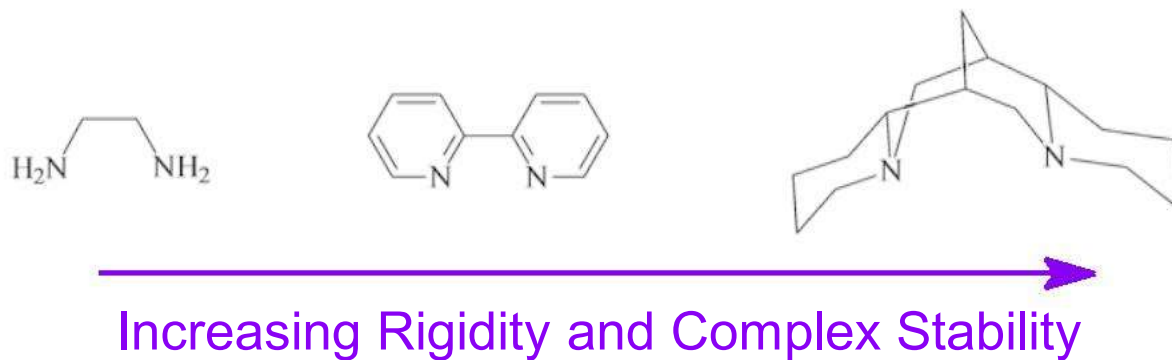
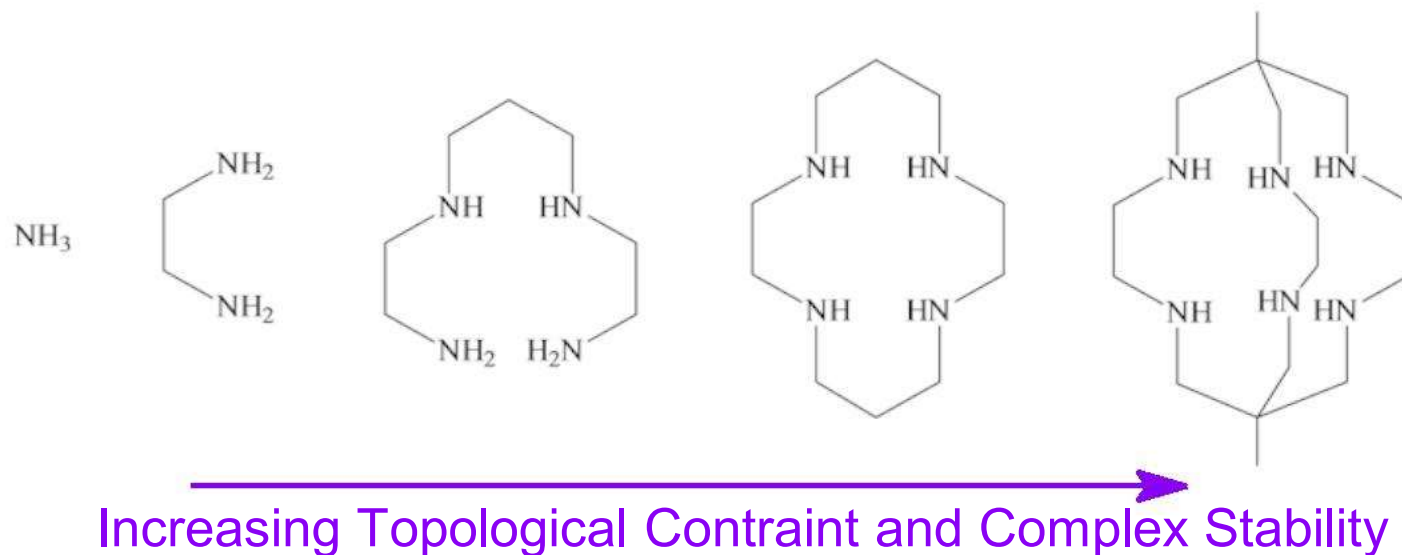
- size
- geometry
- electronics



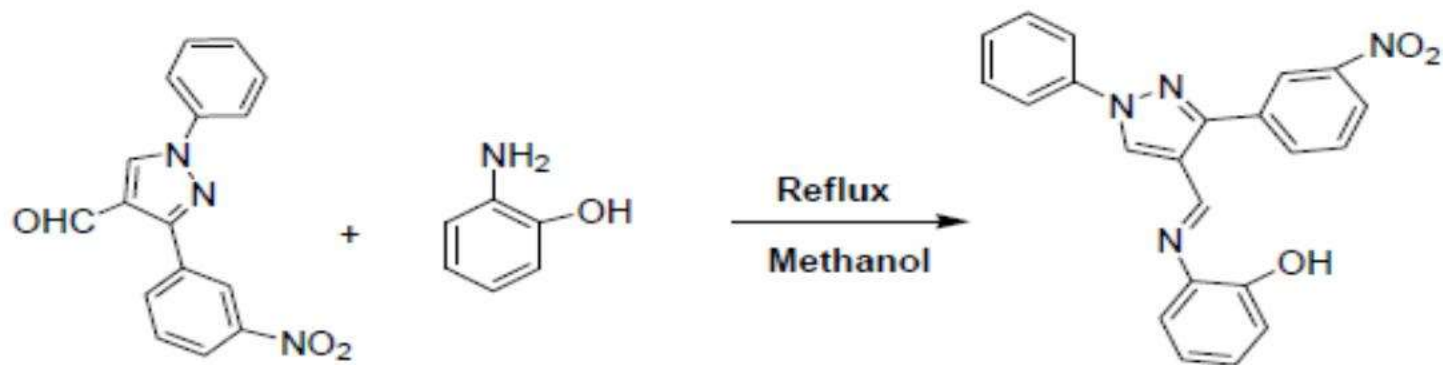
- ***Constraint***: factors reducing freedom in ligand systems and leading to optimization of binding affinity if complementarity is maintained

- topology--connectedness of donor atoms in a ligand
- rigidity--inflexibility or fixedness of donor atoms in a ligand

Topological and Rigidity Effects



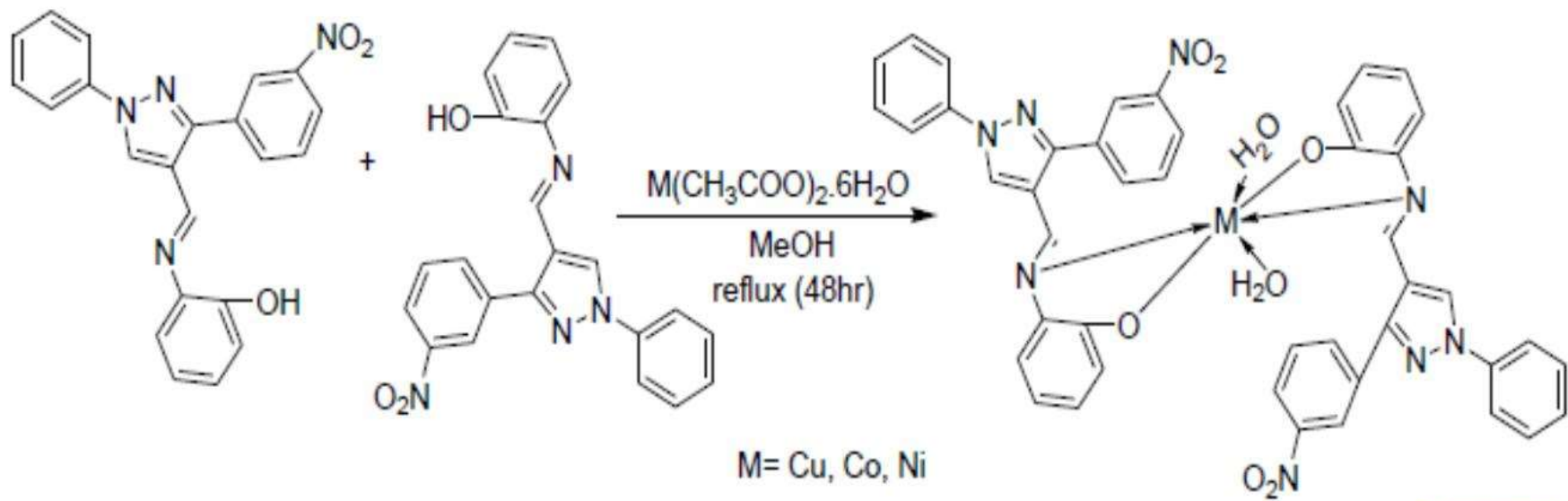
Schiff Base Ligand and Metal Complexes



3-(3-nitrophenyl)-1-phenyl-1H-pyrazole-4-carbaldehyde

2-amino phenol

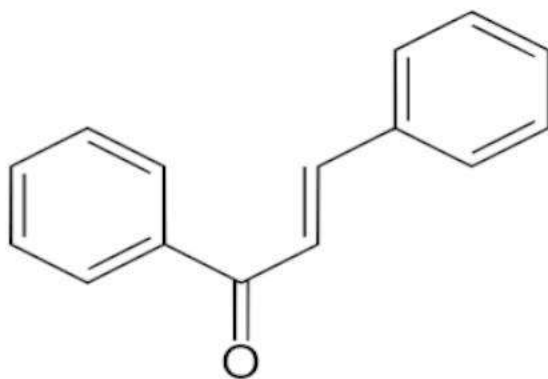
(E)-2-((3-(3-nitrophenyl)-1-phenyl-1H-pyrazol-4-yl)methyleneamino)phenol



Synthesis of Chalcones

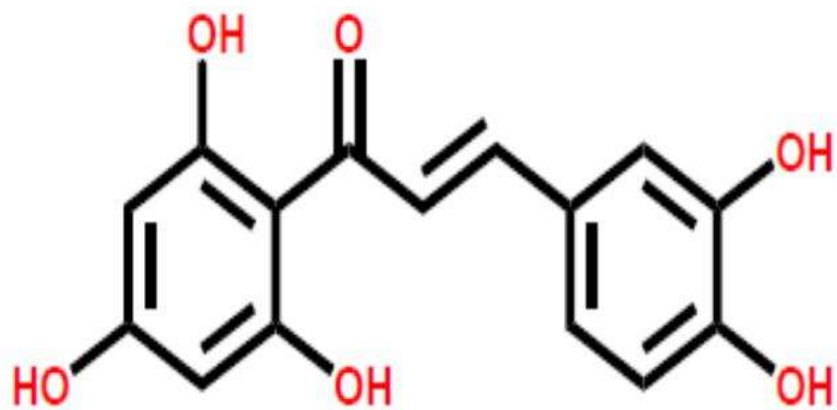
Chalcone is an [aromatic ketone](#) and an [enone](#) that forms the central core for a variety of important [biological compounds](#), which are known collectively as chalcones or [chalconoids](#).

Benzylideneacetophenone is the parent chalcone series. The alternative names given to chalcone are phenyl styryl ketone, benzalacetophenone, β - phenylacrylophenone, γ -oxo- α,γ -diphenyl- α -propylene and α -phenyl- β -benzoylethylene.

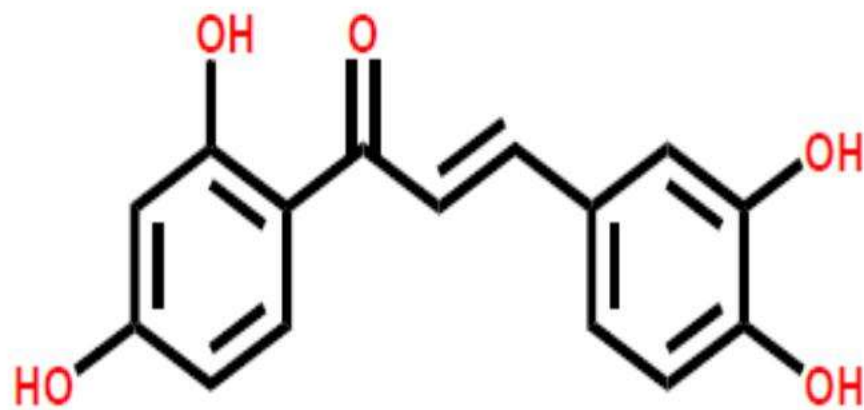


Chalcone

(1,3-Diphenyl-2-propen-1-one)

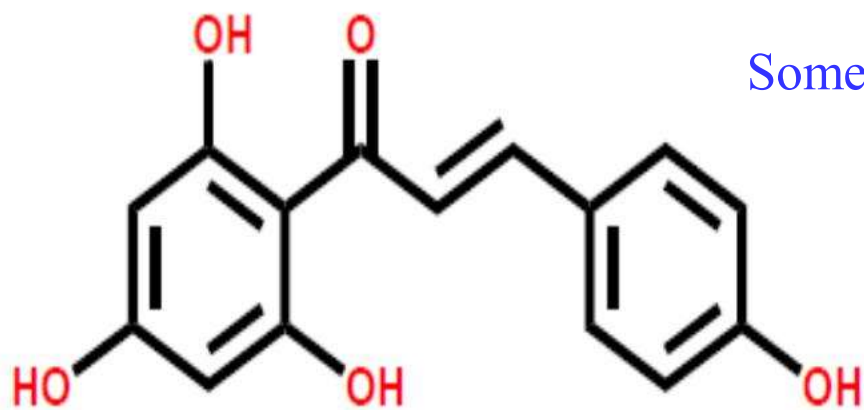


A: 2',3,4,4',6'-pentahydroxychalcone



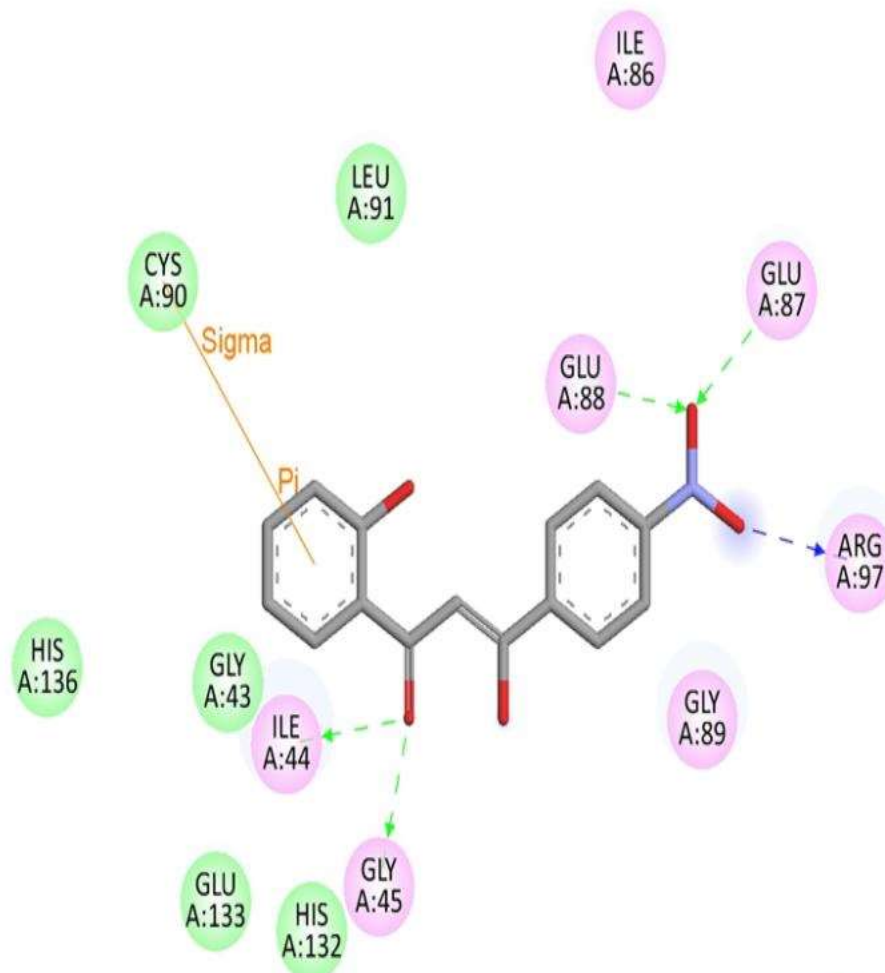
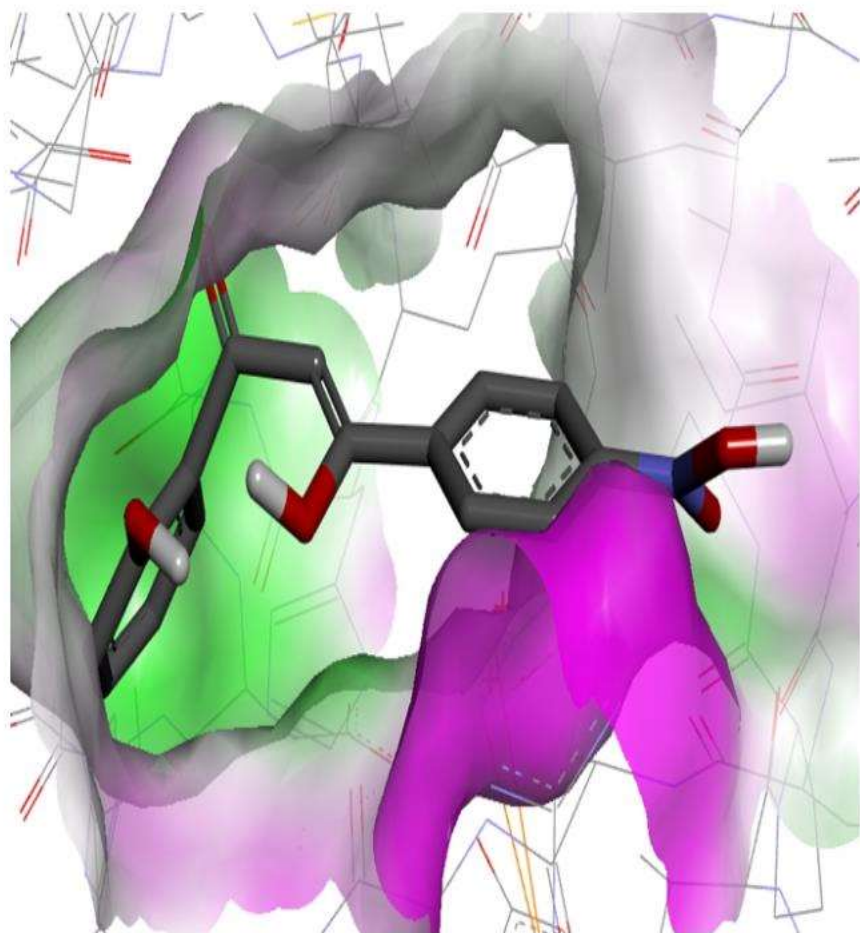
B: 2',3,4,4'-tetrahydroxychalcone

Some New Polyhydroxy Chalcone Derivatives

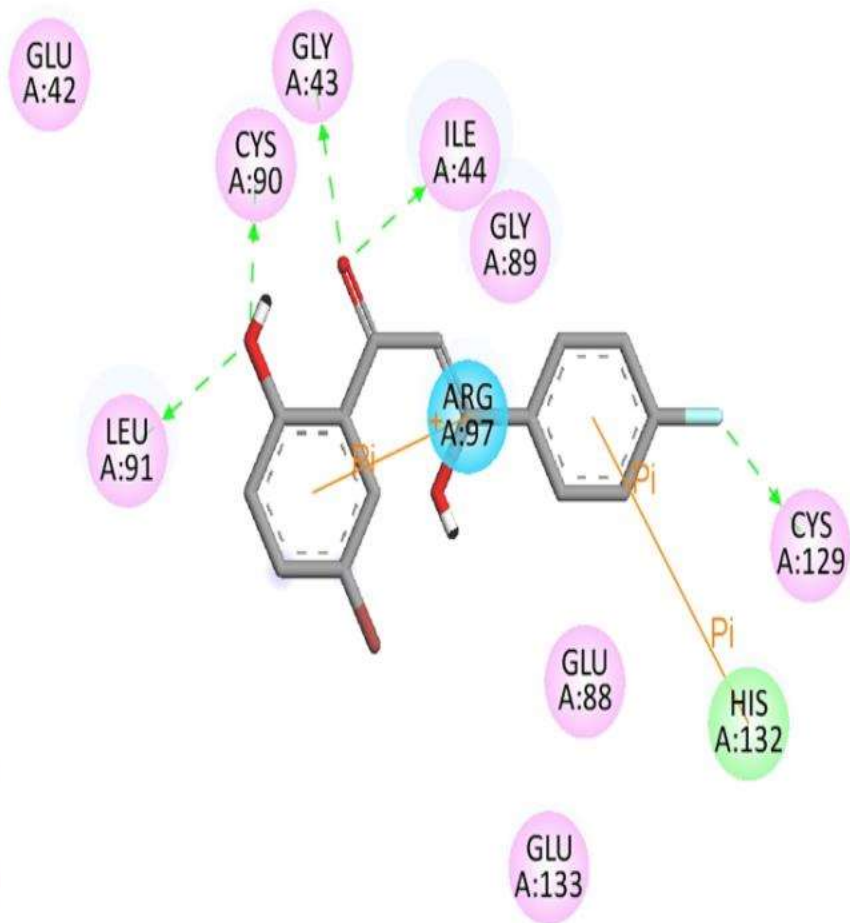
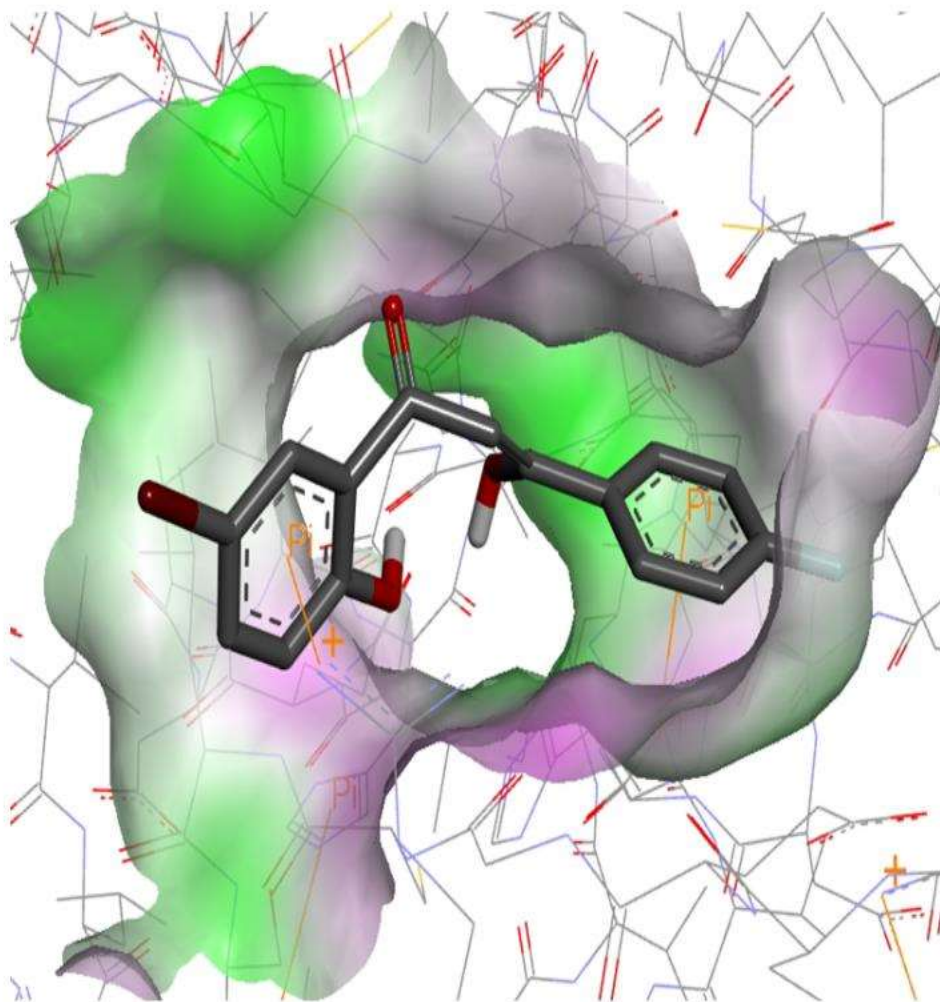


C: 2',3,4',6'-tetrahydroxychalcone

MOLECULAR DOCKING STUDIES OF SOME METAL COMPLEXES

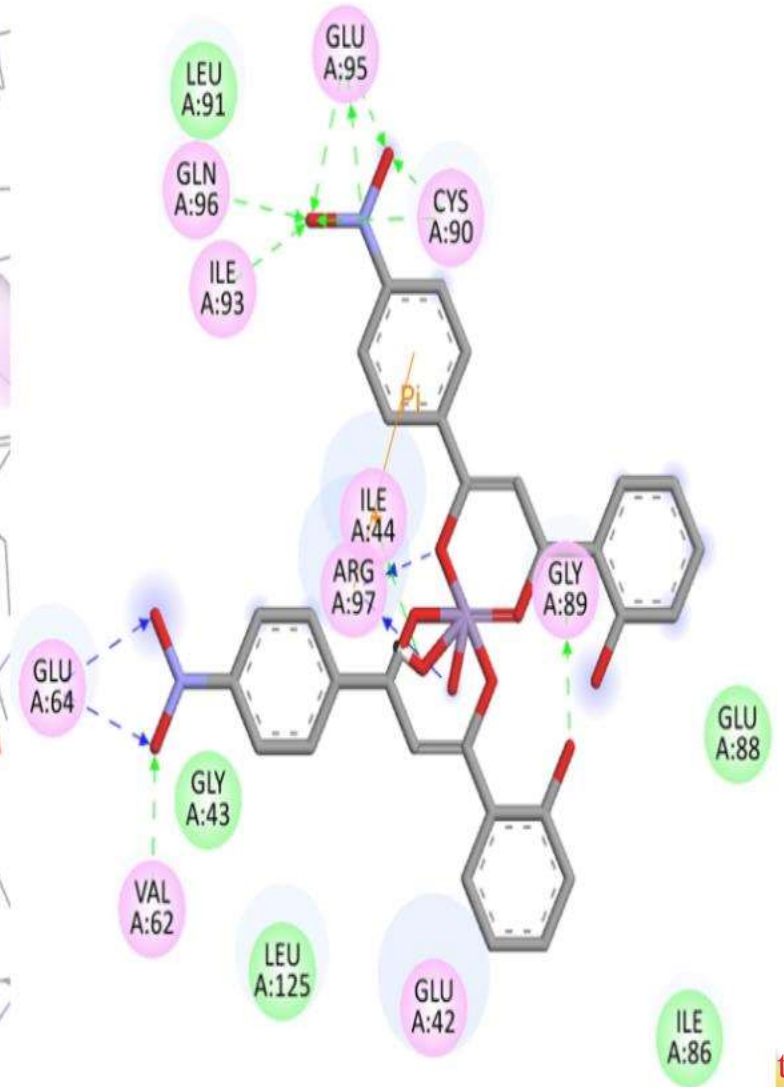
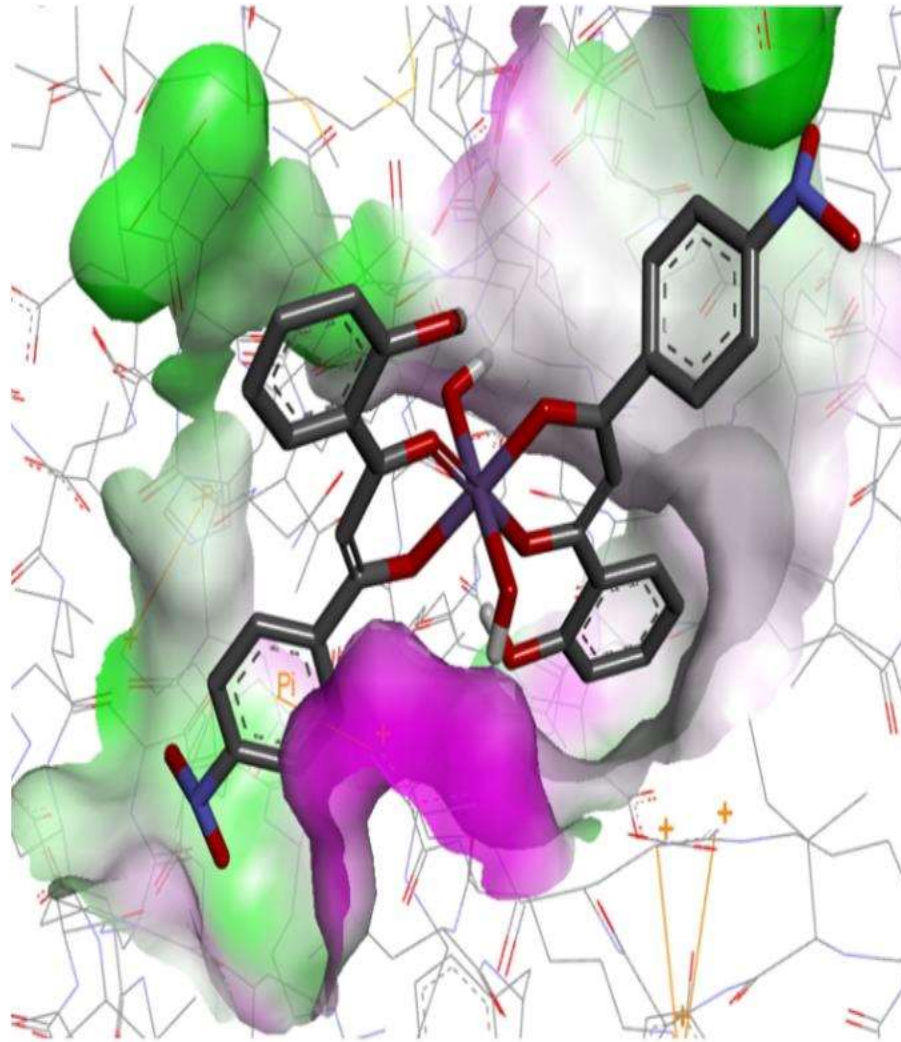


Bound pose of ligand interaction diagram



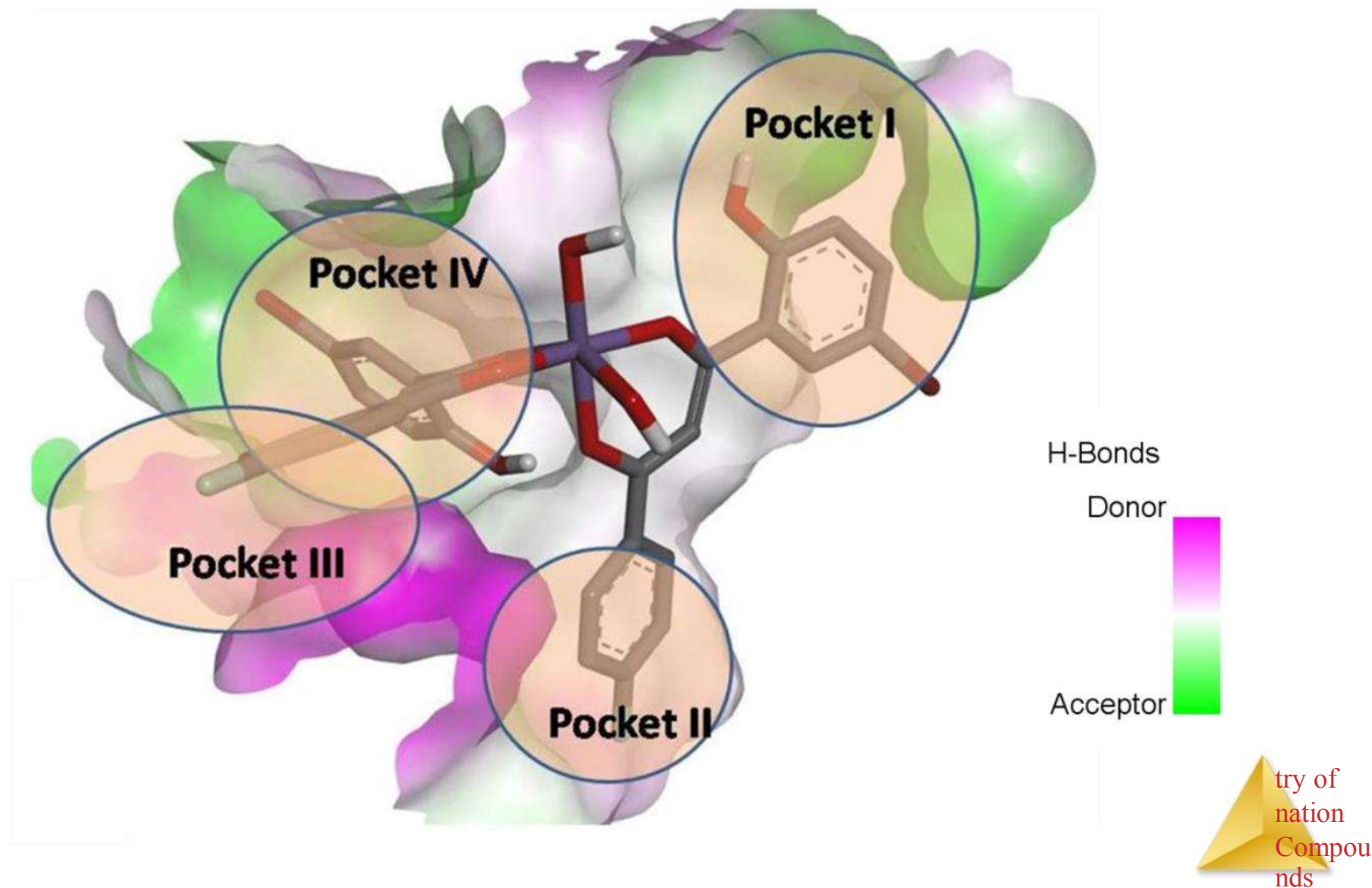
Bound pose of ligand interaction diagram

MOLECULAR DOCKING STUDIES OF SOME METAL COMPLEXES



try of
Coordination
Compounds

Binding pockets in the *E. coli* peptide deformylase enzyme

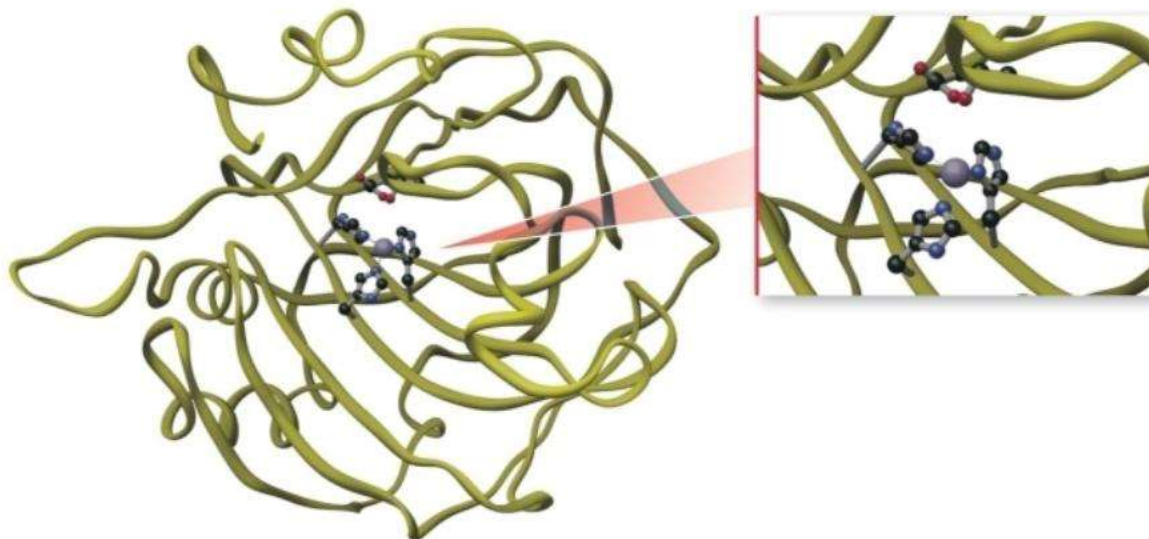


Molecular docking study corroborates the experimental antimicrobial activity specifically against E. coli. In the docking studies against E. coli peptide deformylase enzyme, the importance of ligand complex's access to deeper binding pocket is revealed.

These compounds could form the highly interesting combined two or more pharmacophore sites in one molecule. Thus, it is concluded that the compounds were found to possess a broad range of hydrophilic and lipophilic characters, hence indication of favorable bioavailability based on drug likeness.

Applications of Coordination Compounds

- carbonic anhydrase
- catalyzes the reaction between water and CO_2
- contains tetrahedrally complexed Zn^{2+}



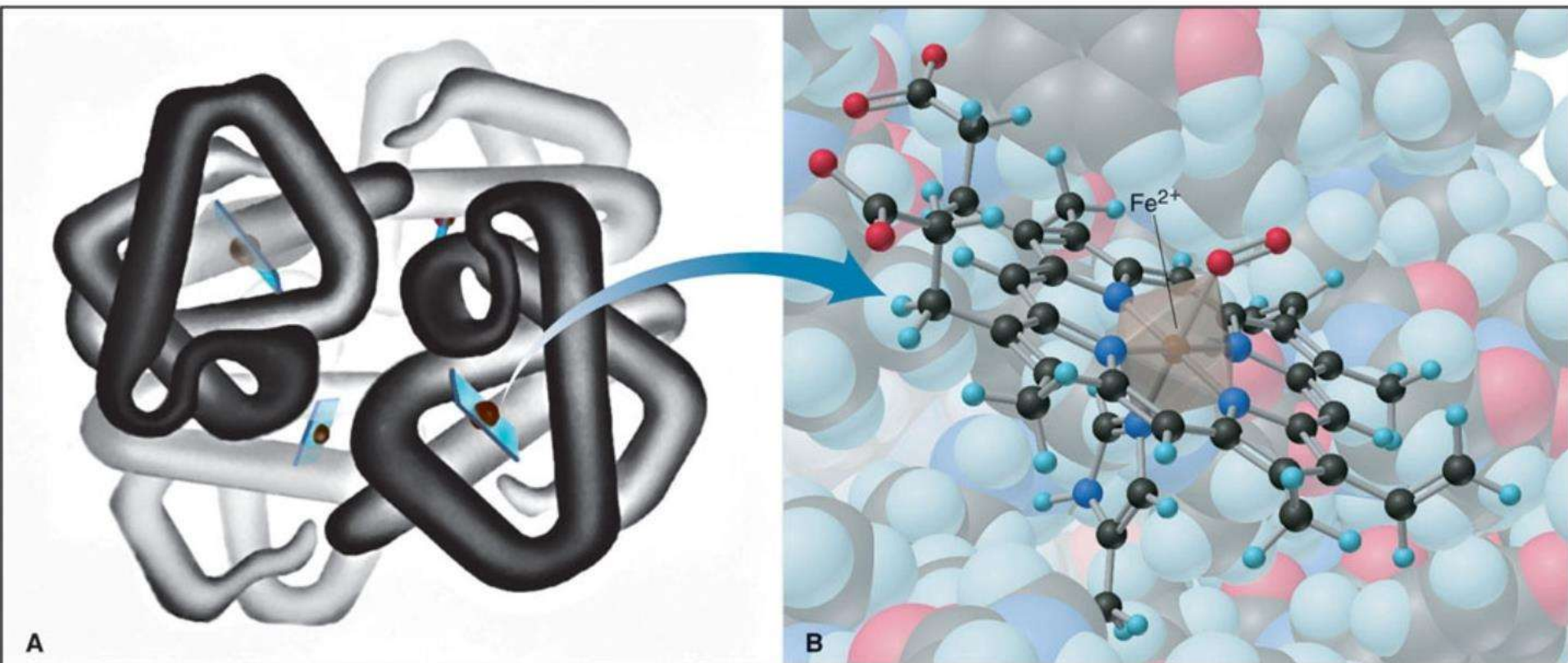
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Tro, Chemistry: A
Molecular
Approach

Chemistry of
Coordination
Compounds

Hemoglobin & Oxyhemoglobin

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Summary

- Overall Goals

Design and synthesize Ligands

Synthesize and characterize transition metal complexes

Evaluate complexes as oxidation catalysts

- * Determine mechanism(s)

- * Redesign Ligands

- Secondary Goals

Understand ligand synthesis.

Apply it to other macrocycles.

Explore coordination chemistry of rigid intermediates.

Quantify solution behavior of ligands. (Proton Sponges)

Overcome proton sponge problem to develop coordination chemistry of cross-bridged ligands

Fully characterize complexes-- structure, spectroscopy, electrochemistry, solution behavior

Current Publications

- Synthesis, spectral characterization and biological screening of potentially active 1, 3-diones and its transition metal complexes, D.M. Suryawanshi^a, V . D. Ingle, N. A. Bhise, A. S. Rajbhoj, **S.T. Gaikwad***, *Chem.Sc.Tra.*5(4), 1042-1048 (2016) DOI:10.7598/cst2016.1285)
 - Synthesis, Spectral characterization and Biological evaluation of 1-(2-hydroxy phenyl)-3-(4-butylphenyl)propane-1, 3-dione as antioxidants agents, Dayanand M. Suryawanshi ^a, Vijayanand D. Ingale^b, Anjali S. Rajbhoj^b and **Suresh T. Gaikwad^{b*}**, *Der Pharmacia Lettre*, 8 (13), 177-181, (2016).
 - Efficient ultrasound synthesis, Spectral studies of 1-(2-hydroxyphenyl)-3-(4-nitro- Phenyl)propane-1, 3-dione with metal complexes as antibacterial and antifungal agents, Dayanand M. Suryawanshi, Vijayanand D. Ingale^b, Anjali S. Rajbhoj^b, **Suresh T. Gaikwad^{b*}**, *Res.J.Chem.Sci.*, 6 (11), 44-47, (2016).
 - Synthesis, Spectroscopic characterization and Antimicrobial activity of selected transition Metal (II) Complexes using Salicylaldehyde and 4-methoxyaniline moiety, Vishal. G. Shinde, Vijayanand. D. Ingale, Dayanand M. Suryawanshi, Anjali. S. Rajbhoj, **Suresh. T. Gaikwad**, *J.Chem.Bio.Phy.Sci.*7(2), 432-436 (2017).
- Synthesis, Characterization and Antimicrobial Screening of 1,3-Dione with their Metal Complexes, SANDEEP N. SAMPAL¹, SHAILENDRA SINGH², V. THAKUR³, ANJALI S. RAJBHOJ³ and SURESH T. GAIKWAD^{3,*}



THANK YOU