جامعة الموصل /كلية التربية للعلوم
الصرفة / قسم الكيمياء
اختياري لاعضوية
ليكندات
المرحلة الرابعة

المحاضرة الاولى

Ligands

- **1- Ligands containing Nitrogen atom:**
- ligands containing Nitrogen as donor atom is must important ligands as electron donor atom and having good ability to coordination with metals ions . With development of the scientific research, various nitrogen-donor ligands have been developed. successfully, the application of nitrogen-donor ligands as well as and its complexes have become an attractive research area. These substances have a variety of structures and properties, and have been widely used in industrial catalysis, life science, material science, pharmacological ....etc

- **Classifications of Nitrogen Ligands**
- According to different classification methods, nitrogen-donor ligands can be divided into chiral nitrogen-donor ligands and achiral nitrogen-donor ligands, as well as monodentate, bidentate, tridentate and polydentate nitrogen-donor ligands. The most common and easy understanding classification way is on the basis of their structure. The details are as follows:
- **1- Amines ligands:**
- The general structure of amine ligand (R- NH2) is a nitrogen atom with a lone pair of electrons. Most primary amines are good ligands and react with metal ions to yield coordination complexes. The amines having many of derivatives like pyrrole, azole and Schiff baces also are good ligands, which can aid metals used in homogenous catalysis.

- **2- Imines ligands:**
- An imine ligand refers to a ligand having a C=N as functional group in its structure, that conceder most common ligands in coordination chemistry. The related ligands like oxime, hydrazone and thiosemicarbazone are also good candidates in coordination chemistry, the complexes produced by them having testability and broad application prospects such as Drugs, catalysis and materials science.
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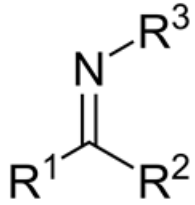

Fig.1 The general structure of an imine

- **- Amids ligands:**
- It is one of Nitrogen ligands that include O=C-NH_2 , as functional group, amid ligands like, nicotine amide, and pyrrolidone may form complexes with metals, those metal complexes in which there is negative charge on the nitrogen in M-N (M refers to metal).
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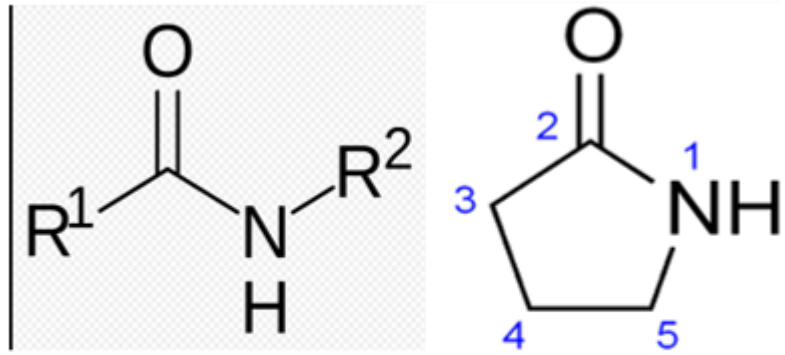
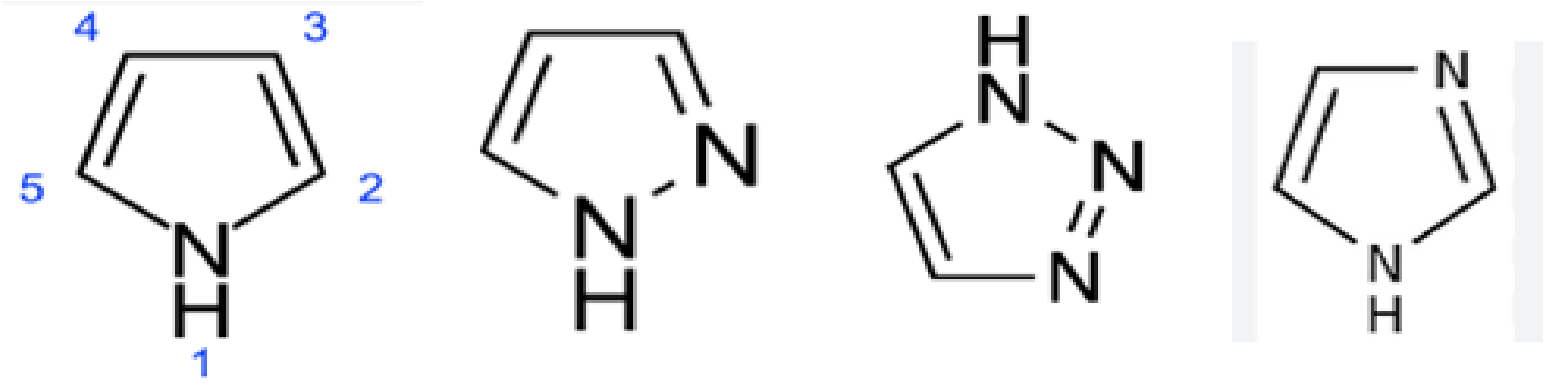


Fig.1 The general structure of amide, and pyrrolidone

4- Azoles ligands (Hetero cyclic)

In this class, the ligands constitute at least five membered ring with one nitrogen as donor atom (called pyrrole) and with two nitrogen's donor atoms may be similar (two nitrogen's together called pyrazol or separated by a carbon called imidazole) and finally with three nitrogen's donor atoms (together called triazole). These above ligands are varied and have broad application



المحاضرة الثانية
ليكندات

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  - **Applications of Nitrogen Ligands**
- Due to the wide variety and special properties of nitrogen-donor ligands, they are widely used in the fields of catalysis, medicine, separation science …etc.
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- **1- Catalysis:**
- Variety of nitrogen-donor ligands combine with a lot of metals provide new dimensions in catalytic homogeneous reactions For examples, amines complexes of Zn, Ru and Ni were used as catalysts for oxidation of epoxides and carbonyl containing organic compounds. Imines complexes with Co, Ni and Pd were used for polymerization of olefins, Cr and Mn imines complexes were used for carbon dioxide addition in styrene and asymmetric epoxidation respectively. Azoles complexes with various metals are used for polymerization, suzuki coupling and for hydrogen aminiation reactions. Substituted porphyrrins complexes are used as catalyst for oxygen evolving reaction and for oxidation of organic compounds
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- **2- medicenes :**
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- Nitrogen ligands can be formed antibacterial drugs showed significant activities against bacteria by structural modifications while antifungal drugs proved to treat skin diseases mainly. The antiviral Nitrogen ligands drugs are currently being used against viral diseases such as influenza, herpes simplex, and HIV.
- **3- industrial felid :**
- Nitrogen-containing ligands and their complexes are important in the industrial field, such as in the paint, paper, and detergent industries.
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- **Classification Of Ligands**

- **1. Ligands containing the nitrogen atom:**
- ligands containing nitrogen as a donor atom are must important ligands as electron donor atoms and having good ability to coordination with metal ions. With the development of scientific research, various nitrogen-donor ligands have been developed. Successfully, the application of nitrogen-donor ligands as well as its complexes has become an attractive research area. These substances have a variety of structures and properties and have been widely used in industrial catalysis, life science, material science, pharmacological, etc

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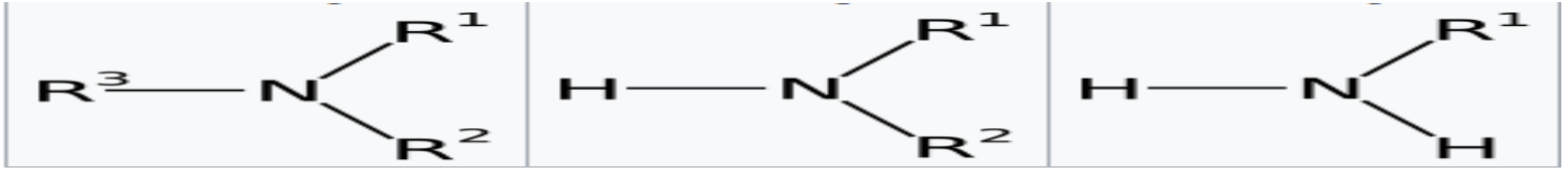

Fig. 1: The general structure of an Amines

- **2- Imines ligands:**
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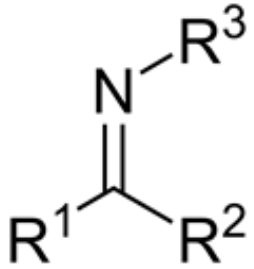

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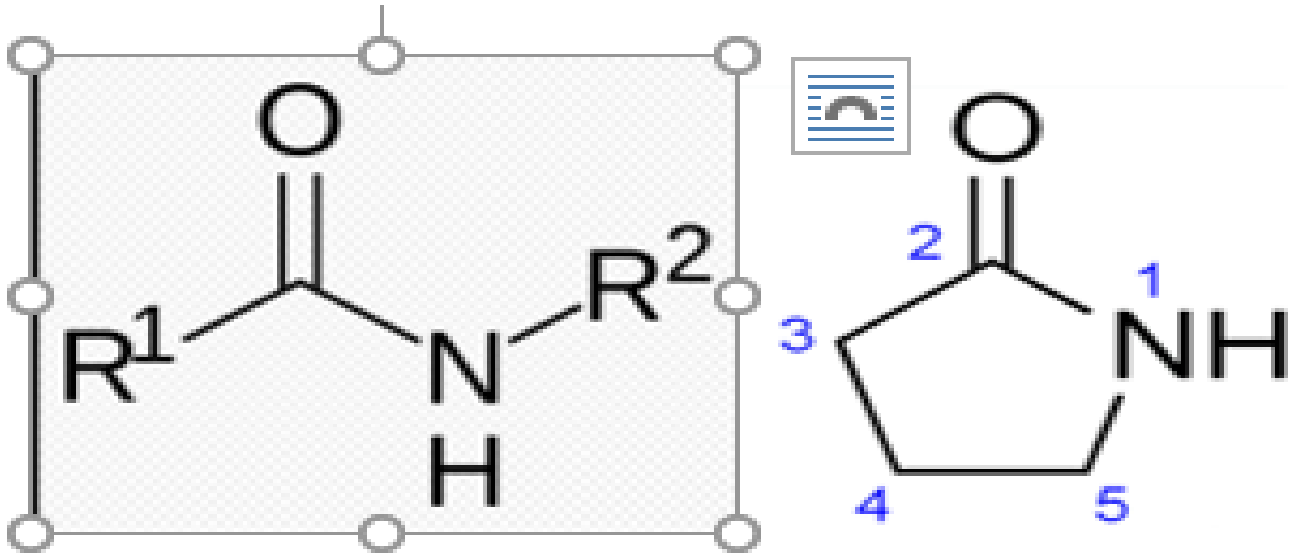
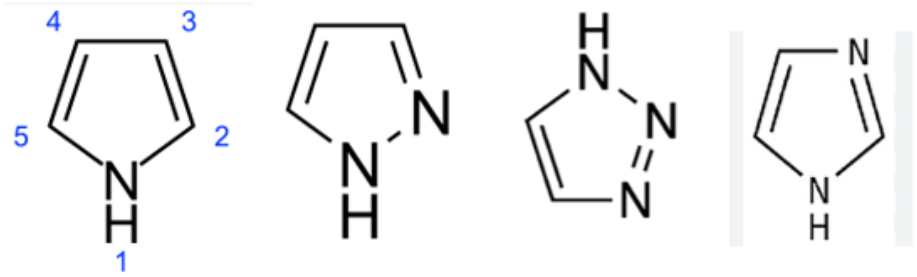


Fig. 3: The general structure of amide and pyrrolidone

- **4: Azoles ligands (heterocyclic)**
- In this class, the ligands constitute at least five membered rings with one nitrogen as a donor atom (called pyrrole), and with two nitrogens, donor atoms may be similar (two nitrogens together called pyrazol or separated by a carbon called imidazole), and finally with three nitrogens as donor atoms (together called triazole). These above ligands are varied and have broad application.



- **Applications of Nitrogen Ligands**
- Due to the wide variety and special properties of nitrogen-donor ligands, they are widely used in the fields of catalysis, medicine, separation science, etc.
- **1- Catalysis:**
- A variety of nitrogen-donor ligands combined with a lot of metals provide new dimensions in catalytic homogeneous reactions. For example, amine complexes of Zn, Ru, and Ni were used as catalysts for the oxidation of epoxides and carbonyl-containing organic compounds. Imines complexes with Co, Ni, and Pd were used for polymerization of olefins; Cr and Mn imines complexes were used for carbon dioxide addition in styrene and asymmetric epoxidation, respectively. Azoles complexes with various metals are used for polymerization, suzuki coupling, Substituted porphyrin complexes are used as catalysts for oxygen evolution reactions and for the oxidation of organic compounds.
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- **2- Medicines:**
- Nitrogen ligands can be formed; antibacterial drugs showed significant activities against bacteria by structural modifications, while antifungal drugs proved to treat skin diseases mainly. The antiviral Nitrogen ligand drugs are currently being used against viral diseases such as influenza, herpes simplex, and HIV.
- **3- Industrial felid:**
- Nitrogen-containing ligands and their complexes are important in the industrial field, such as in the paint, paper, and detergent industries.
- **4- Agricultural fields**:
- Nitrogen ligands and their complexes play an important role in the agricultural field in terms of their use in the production of nitrogen fertilizers, agricultural pesticides, and growth stimulants.

المحاضرة الثالثة
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- **Some of Nitrogen ligands :**
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- 1- A- **Semicarbazide** : its a chemical compound with the formula **$O=C(NH_2)(N_2H_3)$.** It is a water-soluble white solid. It is a derivative of urea.
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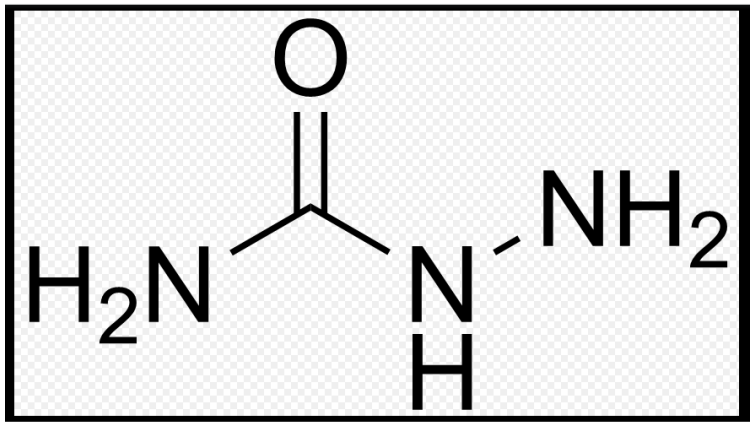

- The compound prepared by treating urea with hydrazine:
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- $O=C(NH_2)_2 + N_2H_4 \rightarrow O=C(NH_2)(N_2H_3) + NH_3$
-
- A further reaction can occur to give carbohydrazide:
- $O=C(NH_2)(N_2H_3) + N_2H_4 \rightarrow O=C(N_2H_3)_2 + NH_3$
-
-
- Semicarbazide is frequently reacted with aldehydes and ketones to produce semicarbazones via a condensation reaction.

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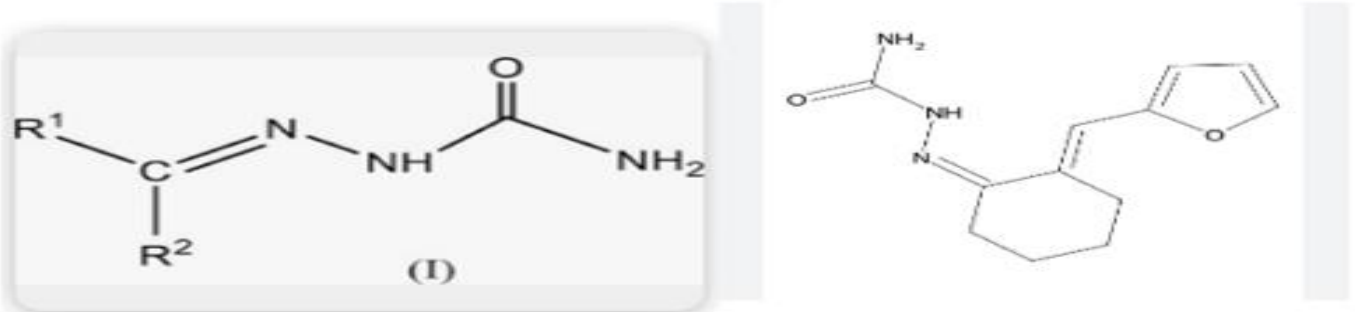
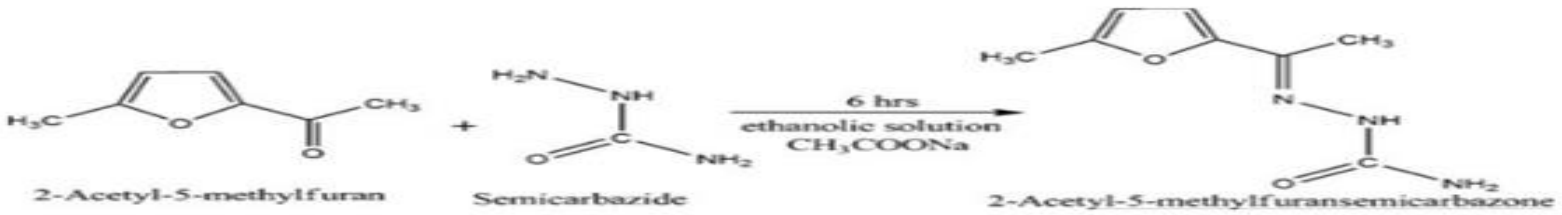
- Semicarbazide products (semicarbazones and thiosemicarbazones) are known to have an activity of antiviral, antiinfective and antineoplastic through binding to copper or iron in cells.





- **B- semicarbazone** :
- If you mix a ketone or aldehyde with semicarbazide, you get imines, which are then formed by a condensation reaction. They are classified as imine derivatives because they are formed from the reaction of an aldehyde or ketone with the terminal -NH_2 group of semicarbazide, which behaves very similarly to primary amines.
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- **from ketones**
-
- $H_2NNHC(=O)NH_2 + RC(=O)R \rightarrow R_2C=NNHC(=O)NH_2$
-
- **from aldehydes**
-
- $H_2NNHC(=O)NH_2 + RCHO \rightarrow RCH=NNHC(=O)NH_2$
-
-
- .

- **Properties and uses:**
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- Some semicarbazones, like nitrofurazone and thiosemicarbazones, are known to fight viruses and cancer. They do this by attaching to copper or iron in cells. Many semicarbazones are crystalline solids, useful for the identification of the parent aldehydes/ketones by melting point analysis. A *thiosemicarbazone* is an analogue of asemicarbazone,e which contains asulphurr atom in place of the oxygen atom.
- Q- What's the difference between semi- and thiosemi-?
- In thiosemi, a sulphur atom replaces an oxygen atom.
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المحاضرة الرابعة
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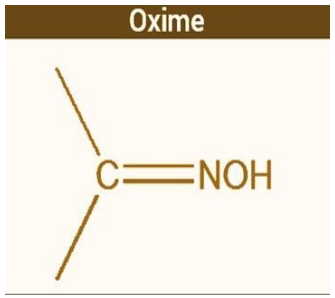
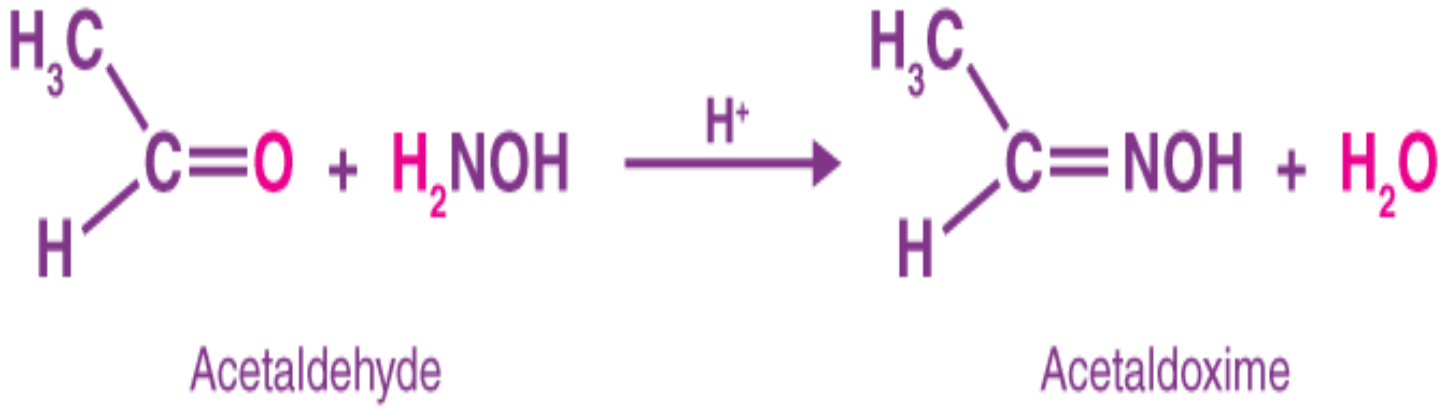
- **Oximes:**
- Oximes are the chemical compounds that belong to the class of imines, having the general formula of [R_1R_2C=N- O H]
- Where R1 is the organic side-chain whereas R2 is the hydrogen, which forms an aldoxime, or like another group of organic compounds such as ketoxime. The O -substituted group of oximes forms a very closely related group of compounds.

- **Oximes Structure**
- Oximes are also called nitrogen possessing organic compounds which are obtained from hydroxylamine, ketone, and aldehyde.
- Oximes that are obtained from aldehydes or called aldoximes can also be dehydrated forming nitriles.
- The other chemical reactions are the conversion of it to amines by treating it with hydrogen or other reducing agents and also by converting it to amides.
- The structure of oxime is a two-sided chain with a central atom consisting of carbon. The two side chains differ entirely from each other. One of the two chains comprises a hydroxyl group.
- Some examples of oximes include Aldicarboxime, aldoxime, dimethylglyoxime, ketoxime, meth oxime, etc.



- **Preparation of Oximes**
- When an aldehyde or ketone reacts with hydroxylamine (NH_2OH) in a weakly acidic medium, it produces oxime and **eliminates water molecules.**
- 1-Acetaldehyde reacts with hydroxylamine forming Acetaldoxime and water.



- 2- Acetone reacts with hydroxylamine and forms Acetoxime and water.
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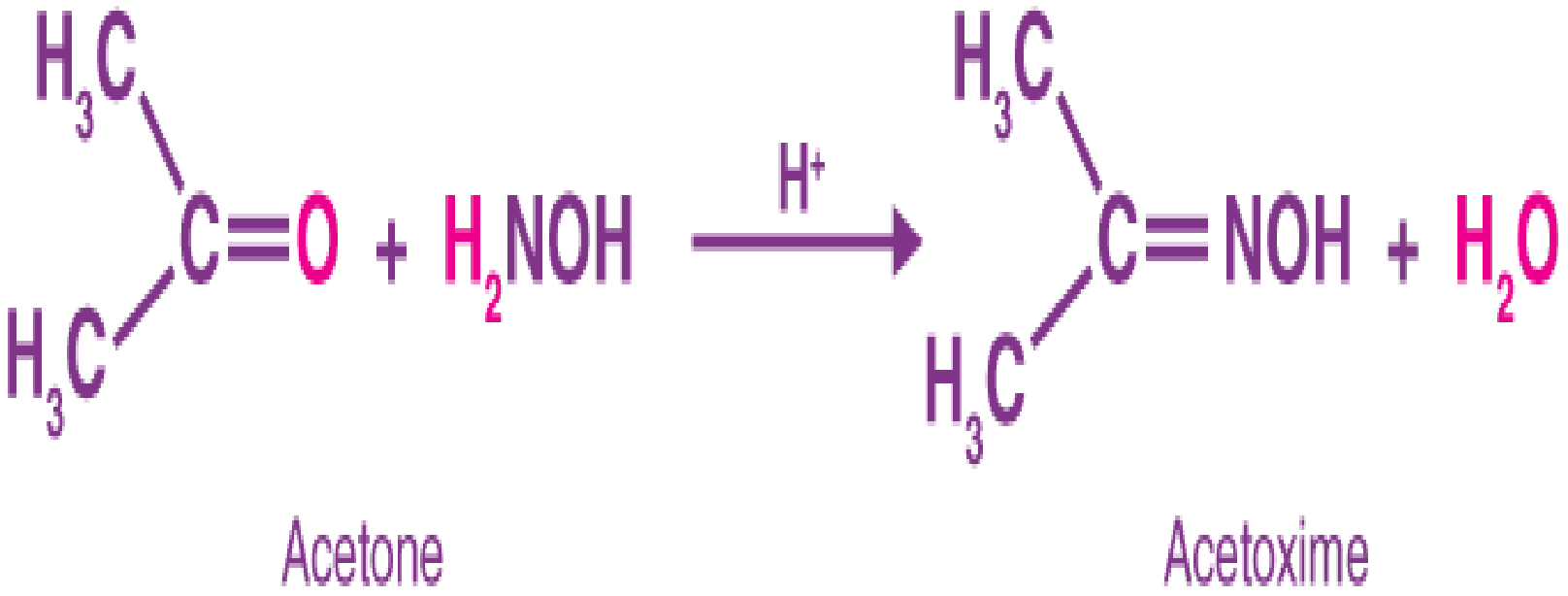
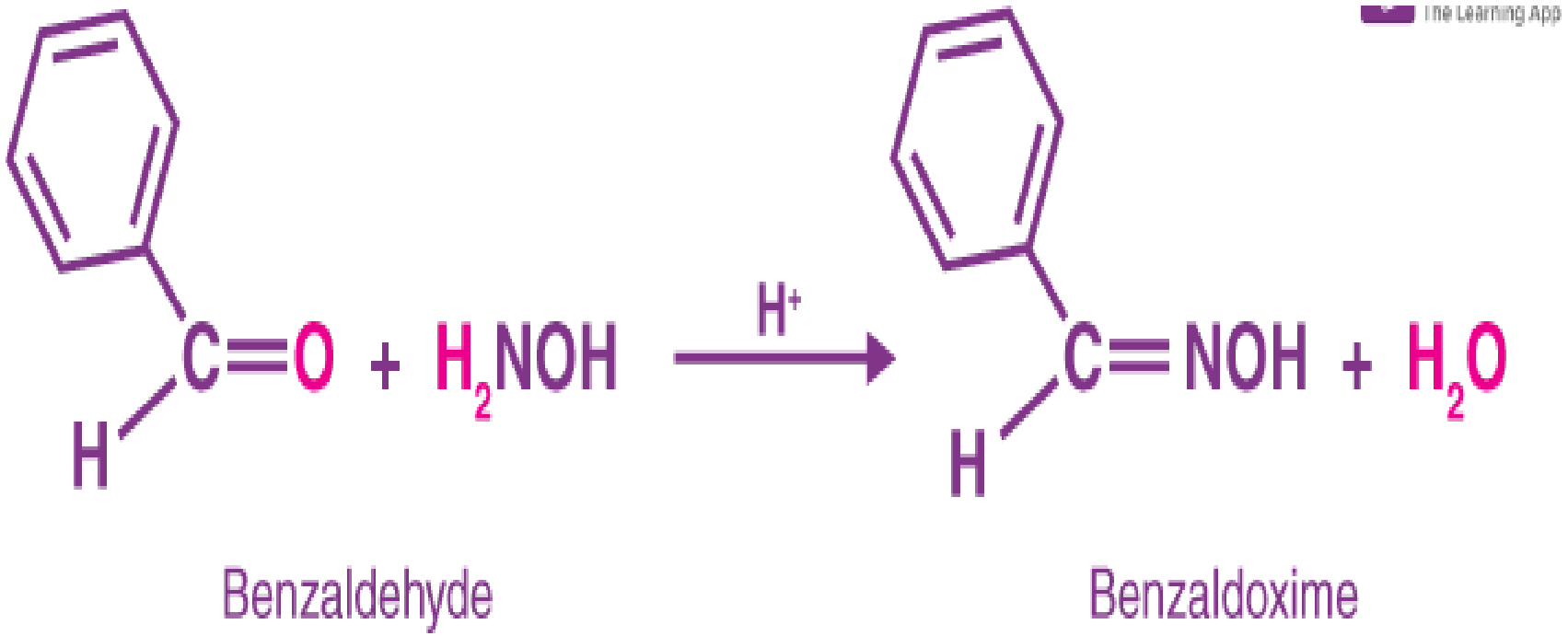


- 3- Benzaldehyde reacts with hydroxylamine and forms enzaldoxime and water.



- **Properties of Oximes**
- Oximes have about 3 characteristics bands with wave numbers measuring 3600 (O-H), 945 (N-O) and 1665 (C=N) in the infrared spectrum.
- The aliphatic group of oximes is resistant to the process of hydrolysis more than the analogous hydrazones.
- These compounds are present in the form of colourless crystals and are said to be less soluble in water.
- Oximes are said to exhibit weak acidic and base properties and are said to be toxic in nature.
- The salts of acids affect the temperature of these compounds.
- Oximes tend to decompose when heated further resulting in a massive explosion.
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- **Applications of Oximes**
- In industries, oximes are used in the production of an organic compound called Caprolactam, which is a precursor for the polymer named Nylon 6.
- In Organic chemistry, these are utilised in catalytic reactions.
- The compounds of oximes are also used as antidotes which are used to serve as nerve agents.
- In Japan, the oxime naming perillaldehyde is used as an artificial sweetener.
- In oil paints, the oxime called Methyl ethyl ketoxime is used as a skinning agent.
- The oxime called Acetone oxime is used as a de-oxidant or a corrosion inhibitor which lowers the toxicity.
- The compound is used in the synthesis of other organic compounds such as cobalt, ketones, etc.

المحاضرة الخامسة
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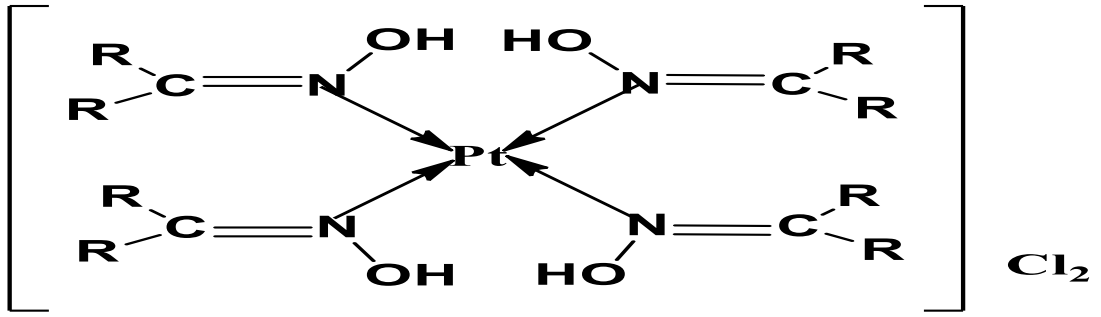
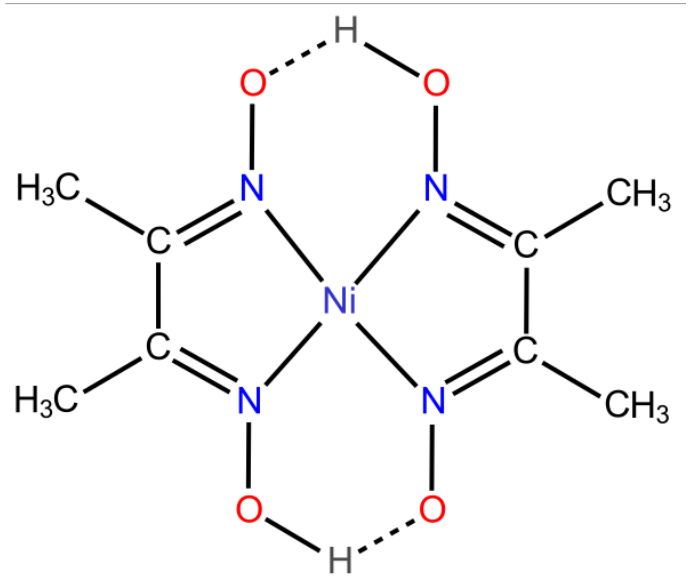
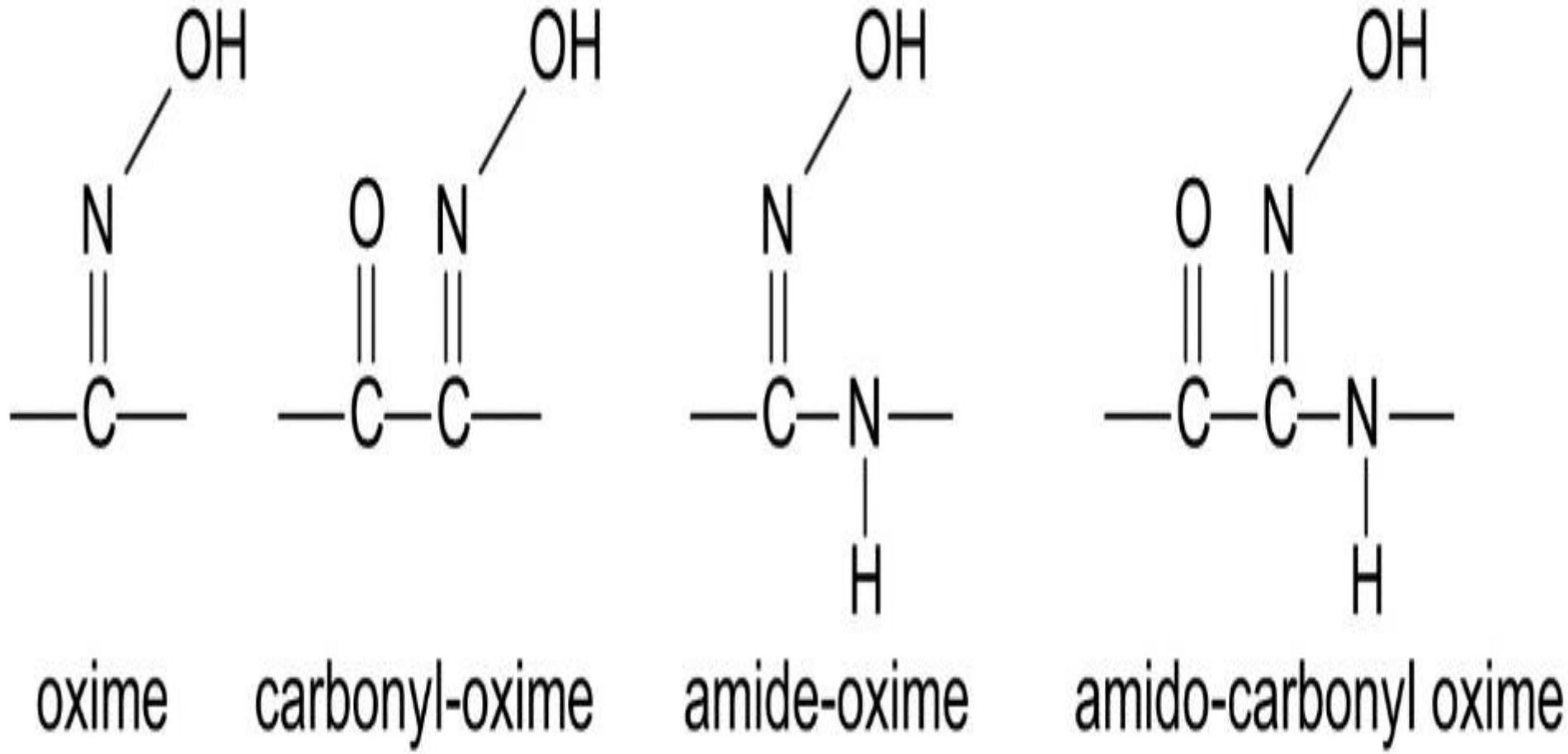
- **- simple oxime**
- The compound is containing one functional group of oxyimine example 4 ligands of oximes coordinate to platinum metal atom as mono dentate ligands Via N atom



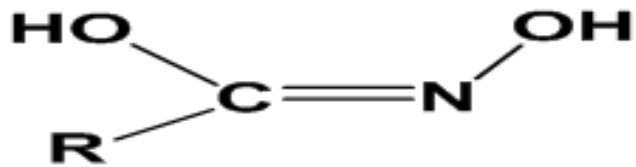
- **2- Dioxime:**
- The best known example is dimethylglyoxime (H_2DMG) which conceder bi-dentate ligand coordinate to Nickel atom as bi-dentate ligands Via Tow N atom. To give red complex used as started materials for cosmetics.



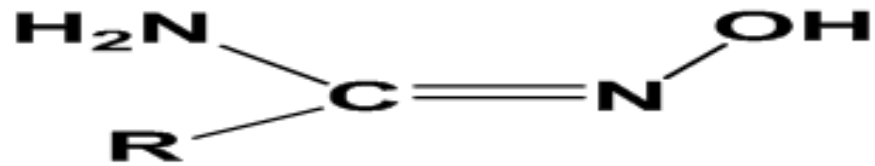
- 3- substituted Oxime
- a- Carbonyl oxime
- b- amide oxime
- c- amido - Carbonyl oxime
- d- hydroxyoxime
- e-Azo oxime



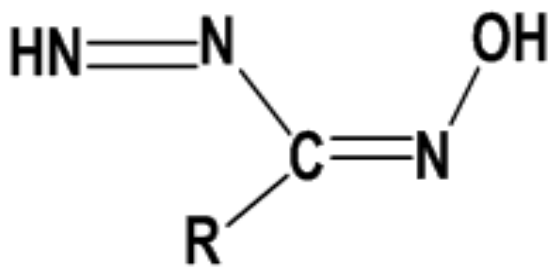
oxime carbonyl-oxime amide-oxime amido-carbonyl oxime



hydroxyoxime



Aminooxime



Azooxime

- Q1
- **Is oxime a functional group?**
- An oxime is a functional group consisting of a hydroxyl group bonded to the nitrogen atom of an imine. An oxime derived from an aldehyde is called an aldoxime and derived from ketone is called ketoxime.
- Q2
- **What is hydroxylamine used for?**
- Hydroxylamine is used as a reducing agent in photography, in synthetic and analytical chemistry, to purify aldehydes and ketones, as an antioxidant for fatty acids and soaps, and as a dehairing agent for hides. In addition, hydroxylamine is used in the production of cyclohexanone oxime or caprolactam.
- Q3
- **Is hydroxylamine water soluble?**
- Hydroxylamine is a polar compound so it dissolves in water.
- Q4
- **Is hydroxylamine toxic?**
- Hydroxylamine is moderately toxic to man, animals, and even plants. However, their toxic reactions become manifest only at concentrations substantially greater than those resulting from normal cell metabolism.

المحاضرة السادسة
ليكندات

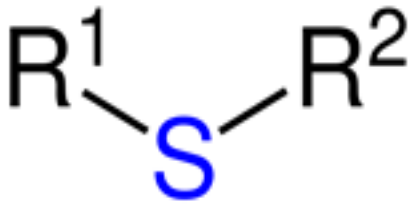
- **Sulfur-Donor Ligands**

- **Sulfur-donor ligands are the compound with sulfur as coordination atom, which belongs to soft base according to hard and soft acids and bases theory (HSAB). Sulfur atom with abundant electrons can bond with metal not only by s and p valence orbitals, but also by d valence orbital, so it can easily form stable complexes with metal ions, especially, with transition metal ions. Because of this property, sulfur atoms in sulfur ligands can be used as σ donors, σ donor-π donors, and σ donor-π acceptors, these bonding modes are related to steric hindrance and valence states of metal ions. For example, the tendency to form π bonds between sulfur and metal centers when the metal is electron deficient or in a high oxidation state. The coordination diversity of sulfur-donor ligands makes it has a wide range of applications.**

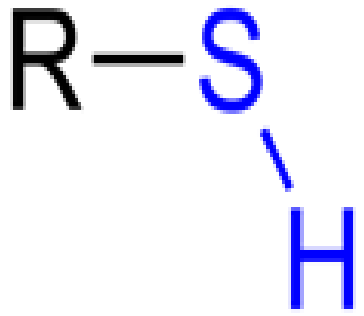
Classifications •

- **According to different classification methods, sulfur-donor ligands can be divided into chiral sulfur-donor ligands and achiral sulfur-donor ligands. The most common and easy understanding classification way is based on their structure, it mainly divided into the following categories.**

- **1- Thioether ligands: An organic thioether or sulfide refers to a functional group in organosulfur chemistry with the connectivity C-S-C. In thioether, sulfur is sp^3 hybridized, in which two valence electrons are bonded with two hydrocarbon groups, and the remaining two lone pair electrons can coordinate with the metal. Due to the electrostatic repulsion and steric hindrance of lone pair electrons of sulfur, the M-S-C (M refers to metal) bond angle in structure of thioether based complexes is usually less than the regular tetrahedron, 109.4°. Alkyl dithioether ligands are representative of sulfide ligands with an earlier research history.**



- **2- Thiol ligands: A thiol is any organosulfur compound of the form R-SH, where R represents an alkyl or other organic substituent. Thiol based metal complexes with various bonding mode and novel geometric configuration, can be used as a potential precursor of a variety of materials, showing a broad application prospect. Among them, the thiol based silver complexes is the most representative, as early as the 1960s, a large number of thiol based silver complexes have been synthesized and has huge application potential in material science, drug research, biochemistry and nonlinear optics fields.**



- **3-Sulfoxides ligands: A sulfoxide is a chemical compound containing a sulfinyl (SO) functional group attached to two carbon atoms. The S=O group in sulfoxide ligands has two kinds of coordination atoms (S and O) with different coordination affinity at the same time, so they have multiple coordination modes. Generally, soft metal ions are easy to coordinate with S. It is worth mentioning that the use of chiral sulfoxides as ligands with transition metals in asymmetric catalysis has vast perspectives and has undergone a long period of development.**

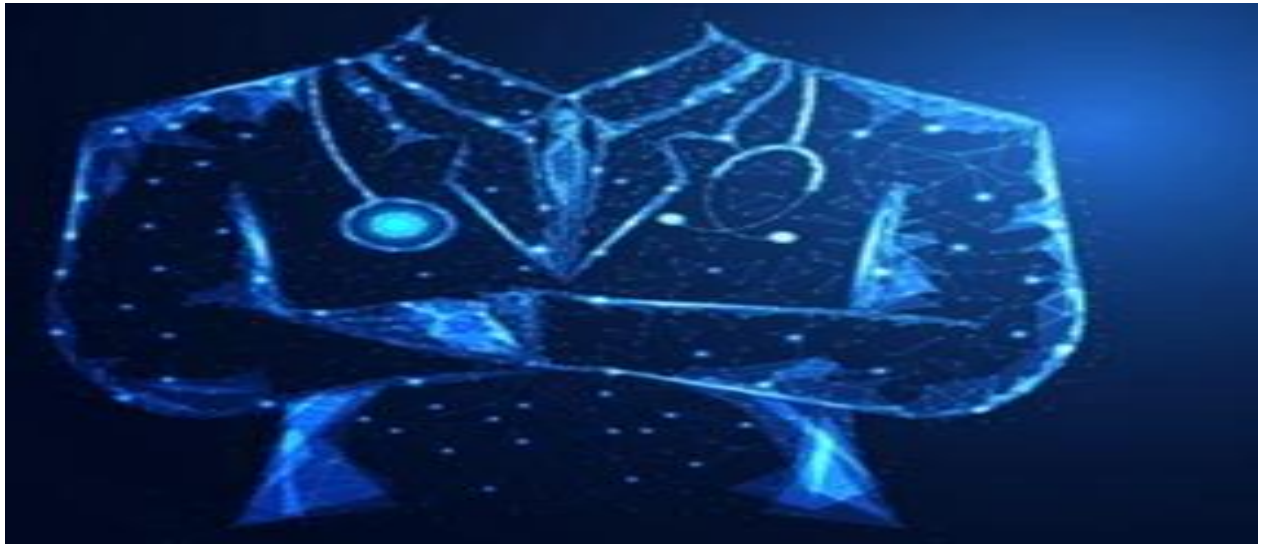
Applications

Sulfur-donor ligands can be coordinated with a variety of metals including transition metals, main group metals, precious metals and *etc*., the resulting complexes are widely used in the fields of catalysis, medical fields, biochemistry and others.

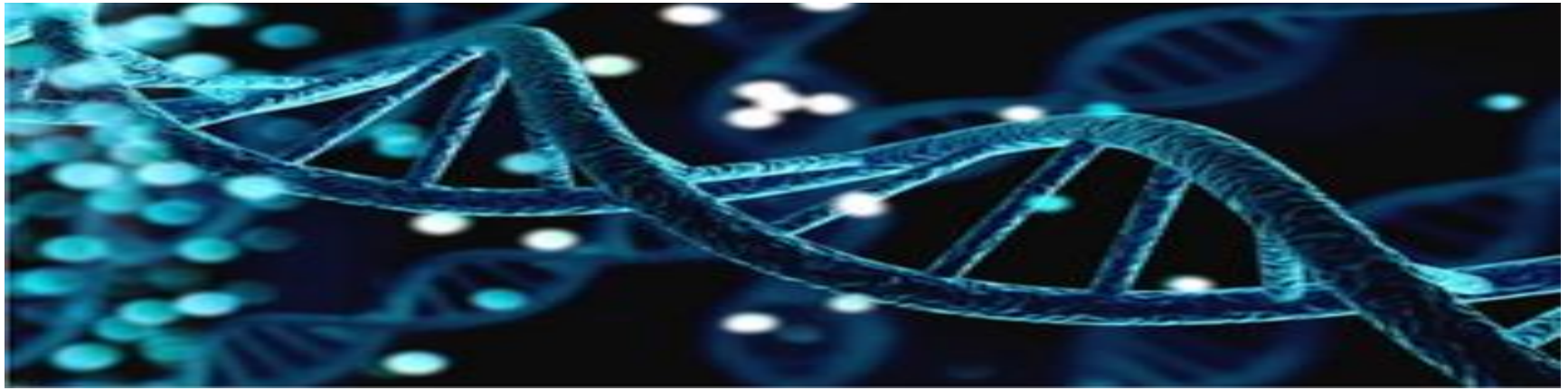
1- Catalysis:

The catalysis of sulfur based metal complexes are mainly related to heterogeneous catalysts. Except for heterogeneous catalysis, complexes by synthesis of chiral sulfur-donor ligands are extensively applied in asymmetric catalysis. The most commonly used ligands are sulfoxides, sulfinamides, N-sulfinyl ureas, and sulfox imines, they can catalyze different types of reactions such as allylic substitution, hydrogenation, hydrogen transfer, conjugated additions, addition of organometallic reagents to aldehydes, Diels-Alder reactions, miscellaneous reactions, allylic substitution, cyclopropanation and many others[1].

- **2-Medicine: Ruthenium(III) complexes have emerged as a new class of effective anticancer agents against tumors that proved to be resistant to all other chemotherapeutic drugs currently in clinical use. The Ru complexes containing sulfur-donor ligands exhibit good anticancer activity, for example, Lorena *et al*. synthesized $[Ru(RSDT)_3]$ and $[Ru_2(RSDT)_5]Cl$ complexes with dithiocarbamato ligands, all the complexes were tested for their cytotoxicity on a panel of human tumor cell lines showing highly significant antitumor activity[2].**



- **3-Biochemistry: Transition metal compounds with electron-rich sulfur-donor ligands have attracted extensive research interest because of their close connection with biochemistry, especially in biocatalysis. In the active part of many metalases (transition metal compounds as enzyme) such as nitrogenase and hydroenzyme, the function of transition metal centers is related to sulfur-donor ligands, sulfur-donor ligands not only induce transition metal activity, but also participate in matrix bonding, acid-base activation, or redox processes closely related to active site transformation**



4- Others: In addition, sulfur ligands based metal complexes also play an vital role in other fields such as lubricants, photocatalysis, battery technology, magnetic resonance imaging and so on.

- **Alfa Chemistry can offer all different kinds of sulfur-donor ligands and related technical advices and services, please don't hesitate to contact us if you are in need of assistance**