❖ Addition Compounds: Crown Ether Complexes and Cryptands, Inclusion Compounds, Cyclodextrins

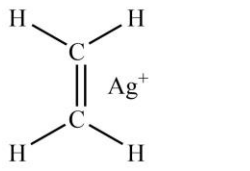
In this section, we will discuss some organic compounds in which the strength of the bonds is less than a typical covalent bond. One of the major types of compounds having weak non-covalent interaction is addition Compounds. An adduct, or addition compound, may simply be defined as the product of the direct addition of two or more distinct molecules, resulting in a single reaction product containing all atoms of all components. Now there are many types of addition compounds but we will confine our discussion only on adducts with bonds weaker than covalent such as electron donor-acceptor complexes.

➢ *Electron Donor-Acceptor Complexes*

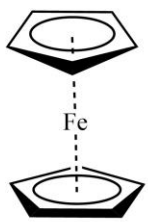
An electron donor-acceptor complex, or simply the charge-transfer complex (CT complex), is an association of two or more molecular entities, or of different parts of one big molecule, where a fraction of electronic charge is transferred from one molecular entity to another.

The resulting electrostatic force of attraction delivers a stabilizing drive for the molecular adduct so formed. The source molecule from which the charge is transferred is called the electron donor whereas the charge receiving species is labeled as the electron acceptor. These electron donor-acceptor complexes usually have spectra that different from the sum of the spectra of the individual participating molecules. There are two primary types of electron donor-acceptor complexes.

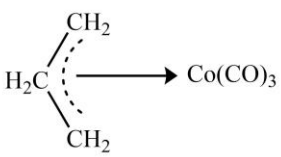
1. When the acceptor is a metal ion and the donor is an aromatic ring an alkene: Some of the typical examples of charge transfer complexes where the donor is an alkene or an aromatic ring and acceptor is a metal ion are given below.



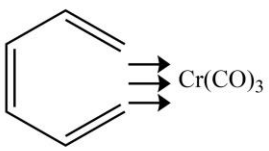
Alkene to metal charge transfer



Ring to metal charge transfer

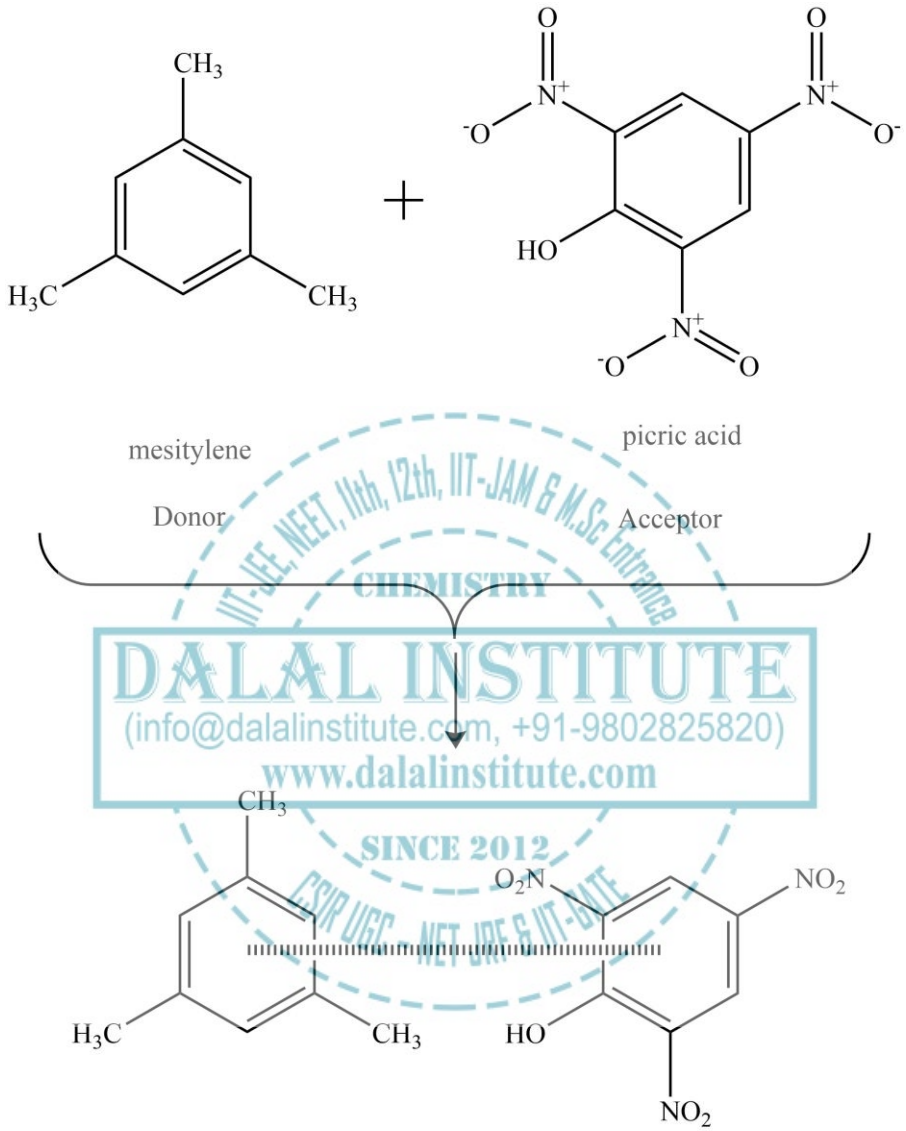


Allyl to metal charge transfer



Open chain to metal charge transfer

2. When the Acceptor is an organic molecule: Some of the typical examples of charge transfer complexes where the acceptor entity is an organic molecule are given below.



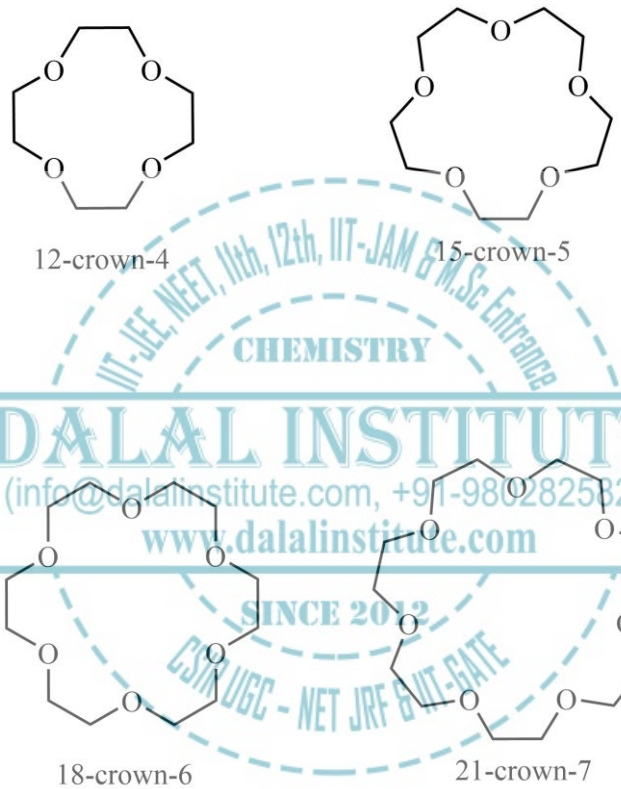
π-complex
(Picrate)

It is also worthy to note that owing to the very small energy gap between the ground and excited states, electron donor-acceptor complexes show absorption peaks in the visible or near-UV region, and therefore, usually show color in sunlight.

➢ ***Crown Ether Complexes and Cryptates***

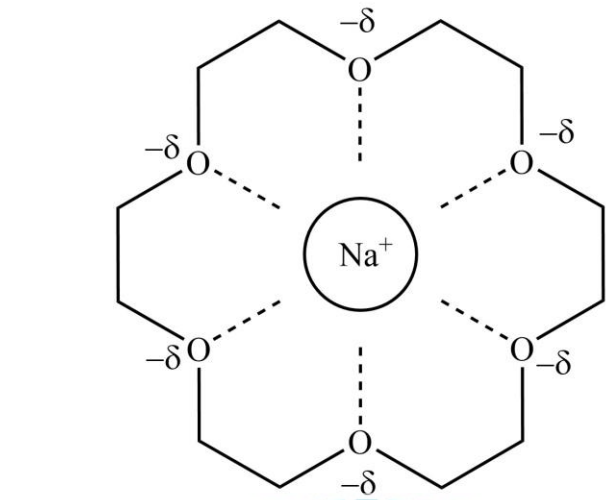
More typical examples of addition compounds are crown ether complexes and cryptands. A general discussion on both these types is given below.

1. Crown ether complexes: Crown ethers may simply be defined as the cyclic compounds that are consisted of a ring with several ether groups. Some of the most common examples of crown ethers are cyclic oligomers of ethylene oxide, where ethyleneoxy is the repeating unit. Chief members of this Crown ethers' series are the hexamer (n = 6), the pentamer (n = 5), and the tetramer (n = 4).

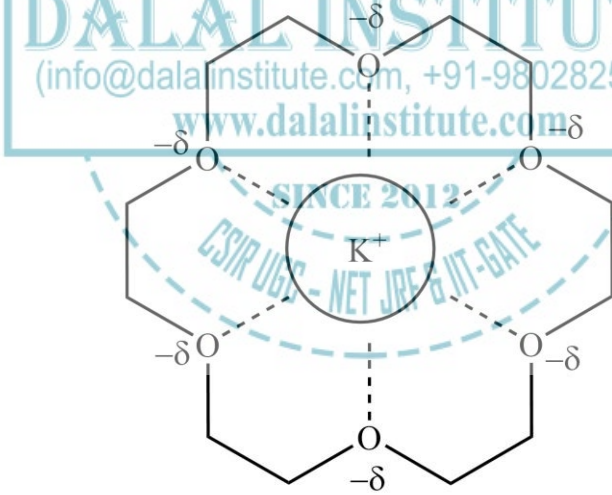


Here the label "crown" means the resemblance with the structure of a king's crown. As far as the nomenclature is concerned, the first number means the number of atoms in the cycle, and the 2nd number means the number of oxygen atoms. Crown ethers are much broader than the oligomers of ethylene oxide; a very important class that is catechols' derivative.

These compounds have a very strong tendency to bind with certain cations, and therefore, generating complexes. The O atoms are well placed to bind with a certain cation situated within the ring, while the ring's exterior remains hydrophobic. The cations thus produced generally form salts that are solvable in non-polar solvents, and therefore, crown ethers are very valuable in the application of phase transfer catalysis. The polyether's denticity affects the affinity of the crown ether for different cations. For instance, 18-crown-6 has more affinity for K^+, 15-crown-5 for Na^+, and 12-crown-4 for Li^+ ion. The very high affinity of 18-crown-6 for K^+ cation is primarily responsible for its toxic character.



Less stable



More stable

It is also worthy to note that crown ethers aren't the only macrocyclic ligands that capable of binding with K^+ cation. Some ionophores like valinomycin also show a very strong preference for the K^+ ion over other cationic species. These compounds have also been known to bind with Lewis acids via σ-hole (i.e., halogen bond) interactions, electrostatic interactions; in other words, bonding takes place between the electrophilic Lewis acid center and the Lewis basic oxygen atoms of the crown ether.

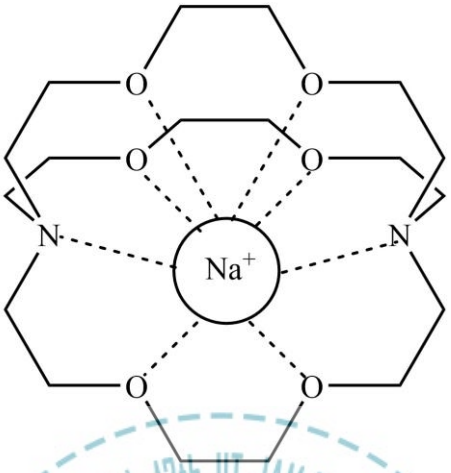
2. Cryptands: Cryptands may simply be defined as a family of synthetic bicyclic and polycyclic multidentate ligands that are capable of binding with a range of cationic species. In 1987, Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen got the Nobel Prize in chemistry for the discovery and finding uses of cryptands and crown ethers, and therefore, starting a novel field of supramolecular studies. The label cryptand means that this ligand gets attached to the substrates in a crypt, burying the guest. These molecular systems are 3-dimensional analogs of crown ethers, nevertheless, are more choosy and have a stronger tendency for complex formation giving lipophilic assemblies.

One of the most commonly studied and important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$; whose IUPAC name is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane. This cryptand is labeled as [2.2.2]cryptand, with numbers inferring about the number of ether groups (and so the binding positions) in each bridge between the nitrogen sites. Numerous cryptands are available commercially by the tradename of Kryptofix. Furthermore, almost all of the amine cryptands show a very high affinity for alkali metal ions, which in turn, made the isolation of salts of K^- possible.

2.2.2]Cryptand

Also, the 3-dimensional void of a cryptand gives a binding site for guest ions, which means it acts as the host for the addition compounds. The complex formed between the guest cation and the cryptand is labeled as a cryptate. These ligands give rise to complexes with numerous hard cations (ammonium ion included), lanthanoids, alkaline earth metals, and alkali metals. Unlike crown ethers, cryptands get attached to the guest ions via both oxygen, as well as, nitrogen sites. This kind of 3-dimensional encapsulation bonding tells us about size-selectivity and enables us to distinguish different alkali ions like K^+ or Na^+ cation.

Cryptands are quite expensive and very problematic to synthesize, nevertheless, very valuable because of better strength and selectivity than their crown ethers counterparts.



More stable Cryptate

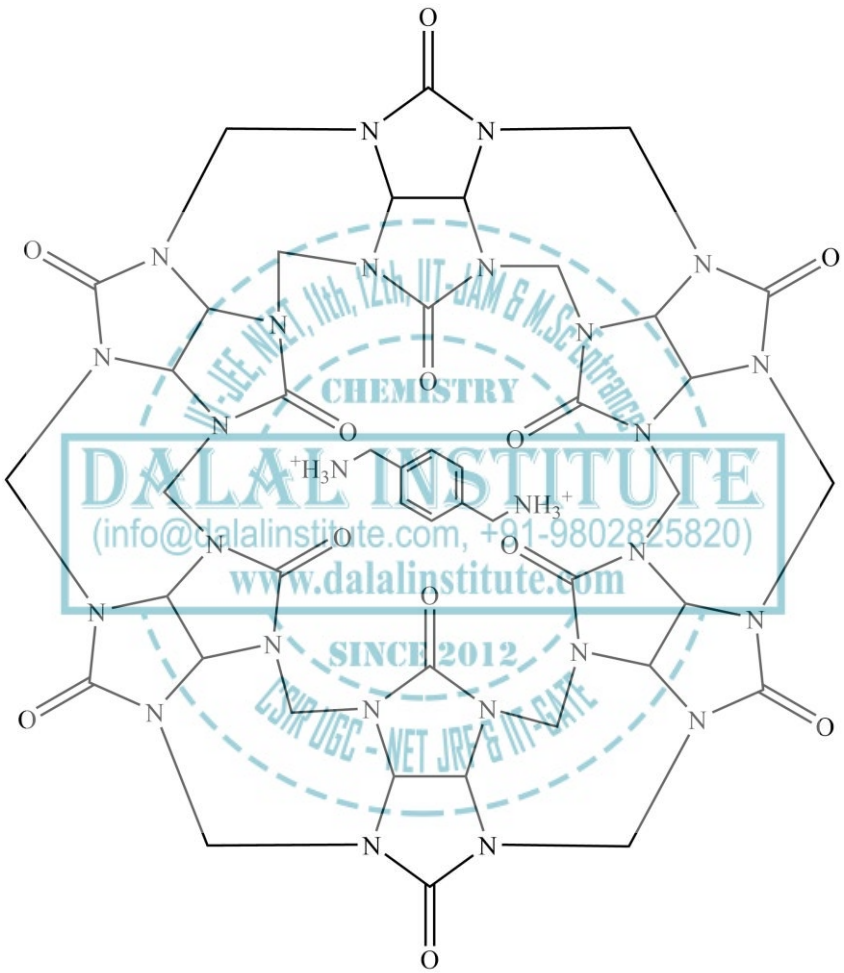
Less stable Cryptate

It is also worthy to note that cryptands are also capable of binding with insoluble salts into the organic phase, making them quite useful as phase transfer catalysts like crown ethers. These ligands enabled the preparation of the electrides and alkalides, and have also been employed to crystallize Zintl ions like Sn_9^{4-}.

➢ ***Inclusion Compounds***

An inclusion compound in host-guest chemistry may simply be defined as a complex where one compound provides a void to accommodate the other.

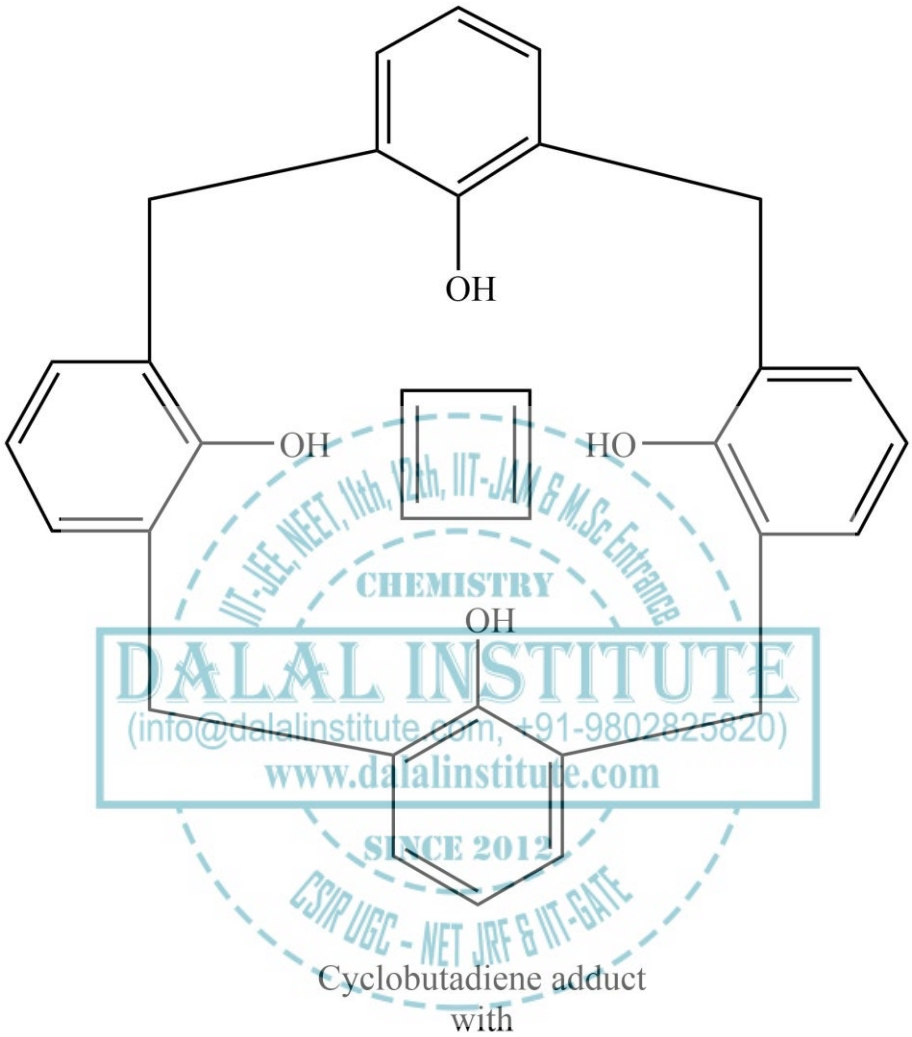
The bonding between the guest and host molecules is purely van der Waals interactions. The idea of inclusion compounds is quite broad, including the channels created between molecules in a crystal lattice where the guest molecules are acceptable.



Inclusion compound consisting of a p-xylylenediammonium bound within a cucurbituril

Calixarenes and associated formaldehyde-arene condensates form an important class of host molecules that can give inclusion compounds. One of the most popular examples is the cyclobutadiene adduct, which would be is unstable otherwise. Cyclodextrins are quite proven hosts for the generation of inclusion compounds. For instance, the ferrocene can be inserted into the cyclodextrin at 100 °C if conditions are hydrothermal.

Cyclodextrin also gives inclusion compounds when treated with fragrances. Consequently, the fragrance molecules have a reduced vapor pressure and become more stable to the exposure to air and light.



Cyclobutadiene adduct with

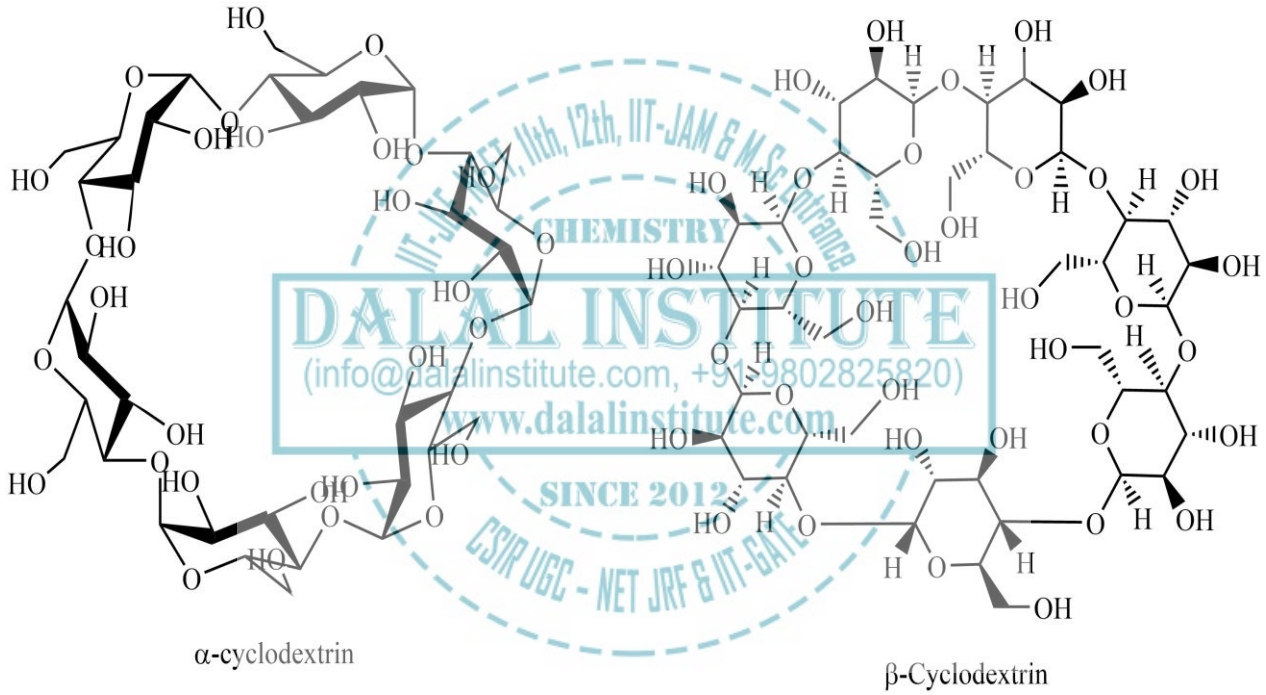
Calix[4]arene-25,26,27,28-tetrol

Furthermore, if incorporated into textiles the fragrance lasts for a longer period because of the slow-release process. Also, crown ethers and cryptands generally don't give inclusion compounds because the guest is bound by attraction forces that are stronger than van der Waals interactions.

It is also worthy to note that if the guest is surrounded in such a way that it is 'trapped', the compound class is known as a clathrate, which is different from than inclusion complex. This encapsulation at the molecular level traps a guest molecule inside another molecule.

- ***Cyclodextrins***

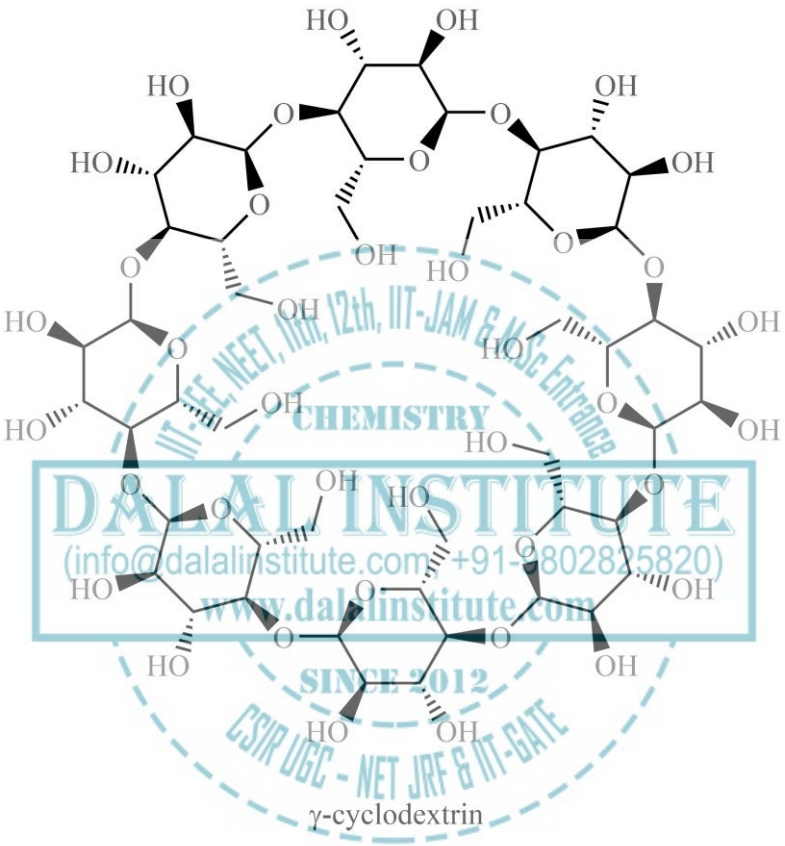
Cyclodextrins may simply be defined as a family of cyclic oligosaccharides which are consisted of a macrocyclic ring having glucose subunits united by α-1,4 glycosidic linkage. These compounds are generated by the enzymatic conversion from starch. Cyclodextrins are quite useful in pharmaceutical, food, chemical industries, and drug delivery, as well as environmental and agriculture engineering. These compounds are made up of 5 or more α-D-glucopyranoside units which are joined at 1->4, like in amylose (a starch's fragment). The biggest cyclodextrin molecule has 32 1,4-anhydroglucopyranoside units, whereas as a poorly characterized mixture, 150-membered cyclic oligosaccharides have also been proved. Archetypal cyclodextrin molecules have several glucose monomer units ranging from 6 to 8 parts in a cycle, giving rise a cone shape structures.



α-cyclodextrin β-Cyclodextrin

With a hydrophilic exterior and hydrophobic interior, these molecules give rise to complexes with hydrophobic systems. The FDA-approved compounds are α-, β-, and γ-cyclodextrin that have been employed for delivery of different kinds of drugs, including prostaglandin, hydrocortisone, itraconazole, nitroglycerin, chloramphenicol. These compounds confer stability and solubility to these drugs. The inclusion complexes of cyclodextrins with hydrophobic fragments can penetrate tissues, and therefore, can be used to release biologically important compounds under explicit conditions. In many cases, the mechanistic behavior of controlled decay of such compounds is based upon the pH change of aqueous solutions, yielding the loss of ionic or hydrogen bonds between the guest and host systems. The other means for the disturbance of the compound take benefit of enzymatic or heating action which is capable to break the α-1,4 bond between glucose monomeric units. These compounds have also been shown to improve mucosal penetration of different kinds of drugs.

Cyclodextrin compounds are synthesized by the enzymatic reaction on starch. Normally cyclodextrin glycosyltransferase is used along with α-amylase. The starch is liquified first either via heating action or by employing α-amylase, then cyclodextrin glycosyltransferase is added for the enzymatic treatment. cyclodextrin glycosyltransferase gives rise to the mixtures of different kinds of cyclodextrins, and therefore, the three main types of cyclic compounds are produced, where the ratios are strongly dependent on the enzyme employed. Also, each cyclodextrin glycosyltransferase has its characteristic ratio of α:β:γ yield.



γ-cyclodextrin

The distillation of the 3 kinds of cyclodextrins takes the benefit of their dissimilar water solubility; β- cyclodextrins is very poorly soluble in water and can be easily obtained via crystallization whereas the more soluble α- and γ- cyclodextrins are typically obtained by using expensive and time-consuming techniques of chromatography. Alternatively, some complexing agents (like acetone toluene, or ethanol) can also be added in the course of the enzymatic treatment step to yield a complex with the desired cyclodextrin, which in turn, can easily be precipitated subsequently. The formation of the complex drives the transformation of starch into the generation of the precipitated cyclodextrin, and so enriching its amount in the final products. W. Chemie practices some dedicated enzymes, that can yield α-, β- or γ-cyclodextrin explicitly. This is quite important particularly in food engineering because the only α-, β- or γ-cyclodextrin can be consumed without any limit on the daily intake.

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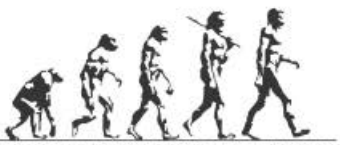

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