27.19
Secondary Structures of Peptides and Proteins

Levels of Protein Structure

Primary structure = the amino acid sequence plus disulfide links

Secondary structure = conformational relationship between nearest neighbor amino acids

- α helix
- pleated β sheet

Levels of Protein Structure

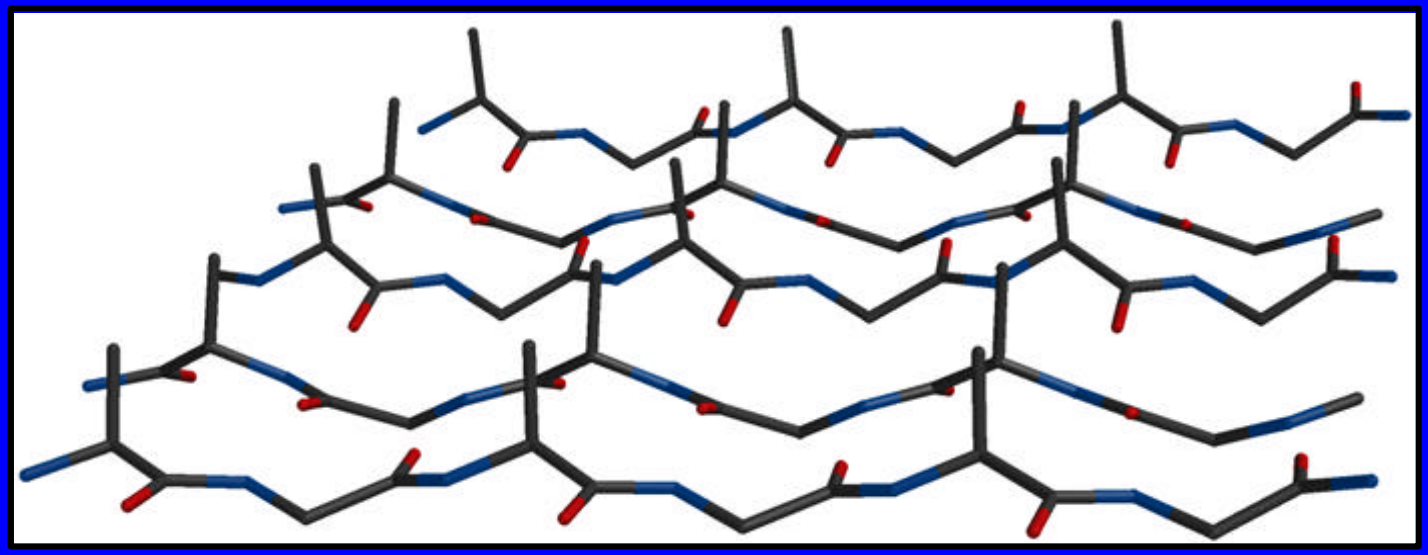
The α-helix and pleated β sheet are both characterized by:

planar geometry of peptide bond

anti conformation of main chain

hydrogen bonds between N—H and O=C

Pleated b Sheet



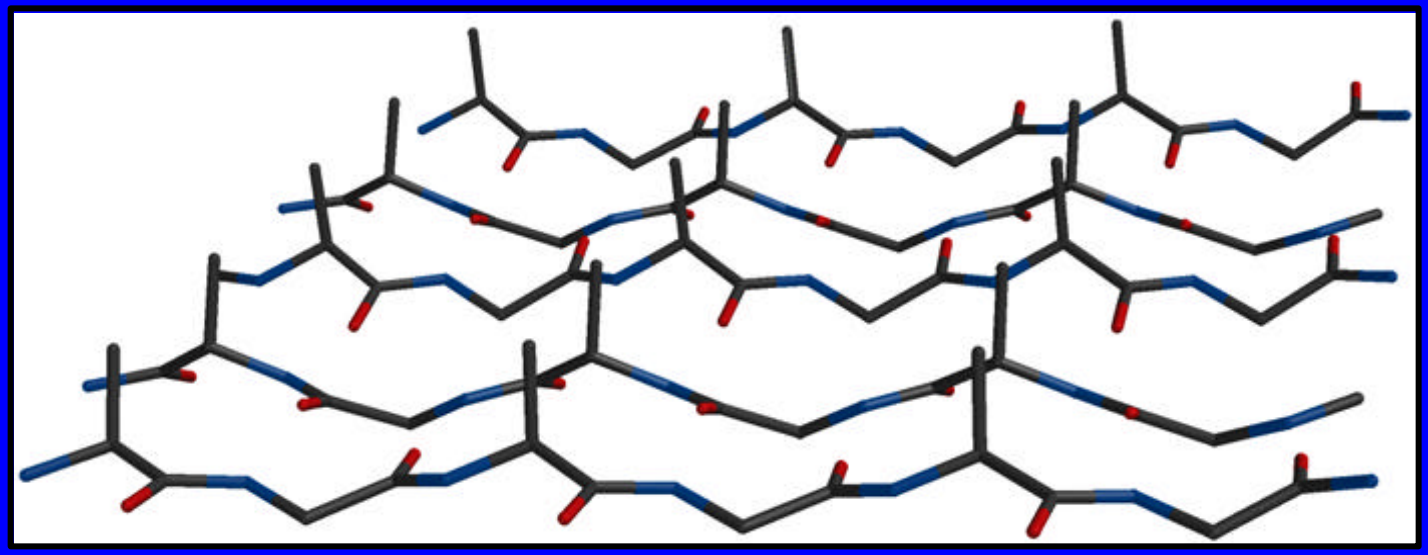
Shown is a β sheet of protein chains composed of alternating glycine and alanine residues.

Adjacent chains are antiparallel.

Hydrogen bonds between chains.

van der Waals forces produce pleated effect.

Pleated b Sheet



β Sheet is most commonly seen with amino acids having small side chains (glycine, alanine, serine).

80% of fibroin (main protein in silk) is repeating sequence of —Gly—Ser—Gly—Ala—Gly—Ala—.

β Sheet is flexible, but resists stretching.

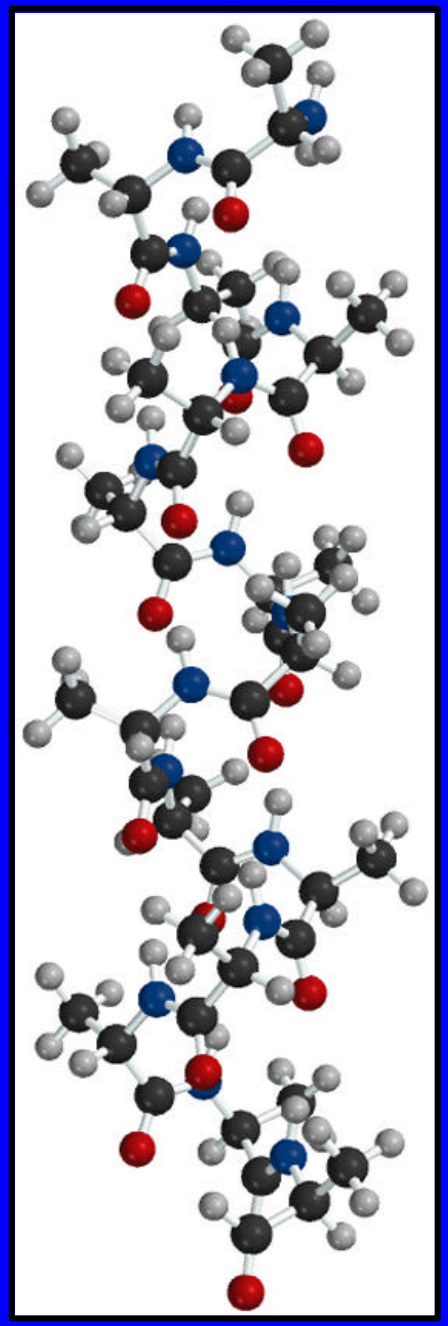
a Helix

Shown is an α helix of a protein in which all of the amino acids are L-alanine.

Helix is right-handed with 3.6 amino acids per turn.

Hydrogen bonds are within a single chain.

Protein of muscle (myosin) and wool (α-keratin) contain large regions of α-helix. Chain can be stretched.



27.20
Tertiary Structure of Peptides and Proteins

Tertiary Structure

Refers to overall shape (how the chain is folded)

Fibrous proteins (hair, tendons, wool) have elongated shapes

Globular proteins are approximately spherical

most enzymes are globular proteins

an example is carboxypeptidase

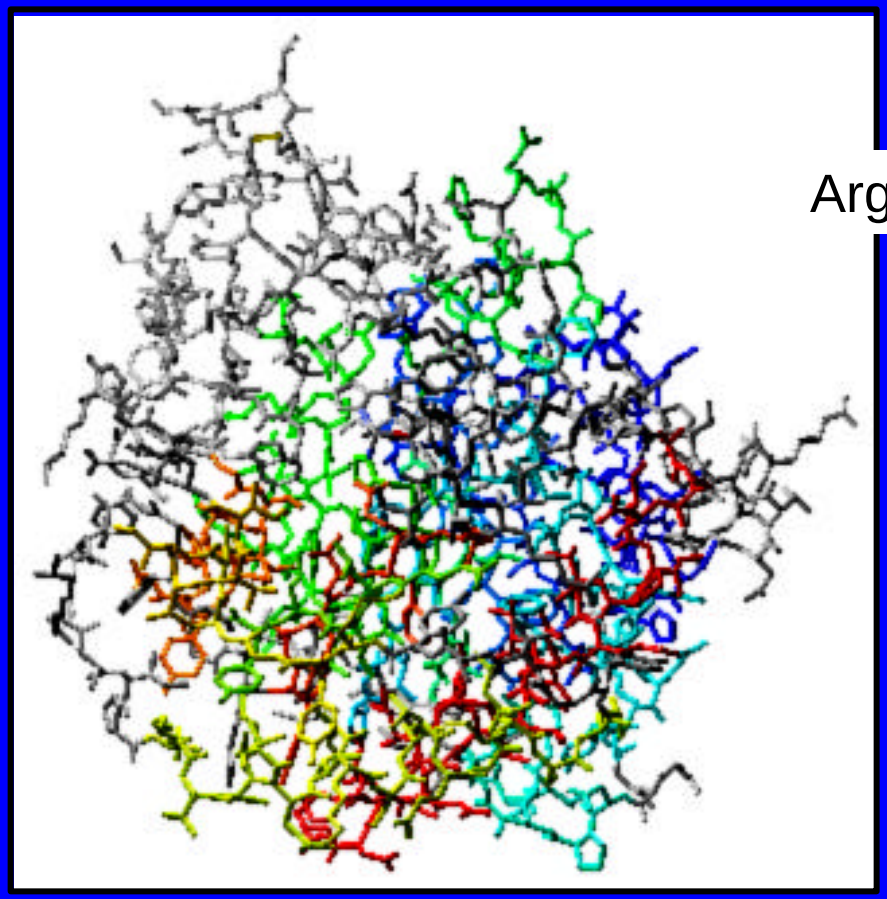
Carboxypeptidase

Carboxypeptidase is an enzyme that catalyzes the hydrolysis of proteins at their C-terminus.

It is a metalloenzyme containing Zn^{2+} at its active site.

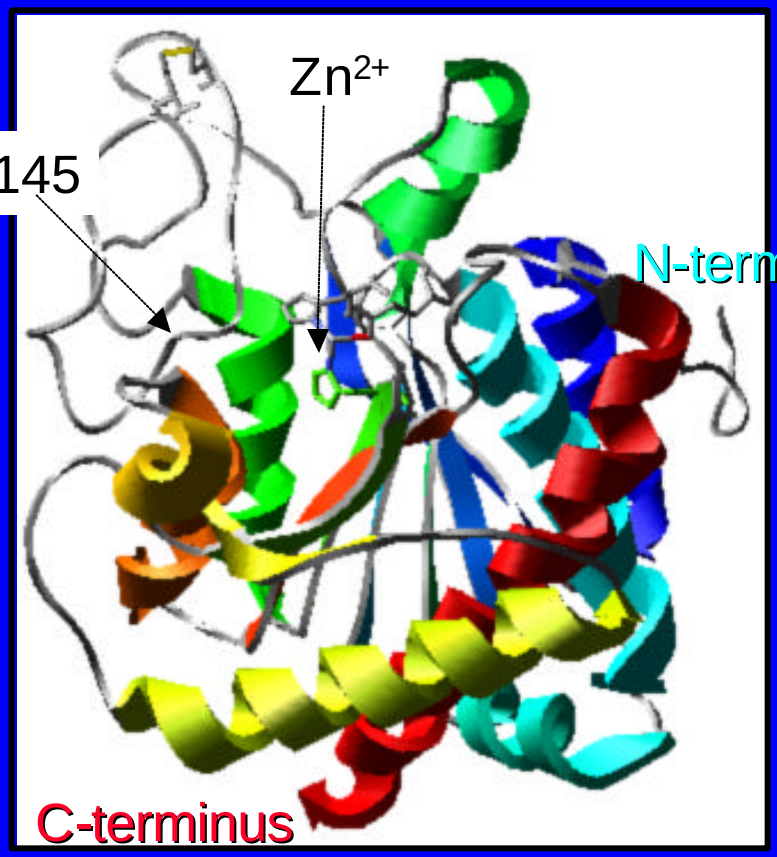
An amino acid with a positively charged side chain (Arg-145) is near the active site.

Carboxypeptidase



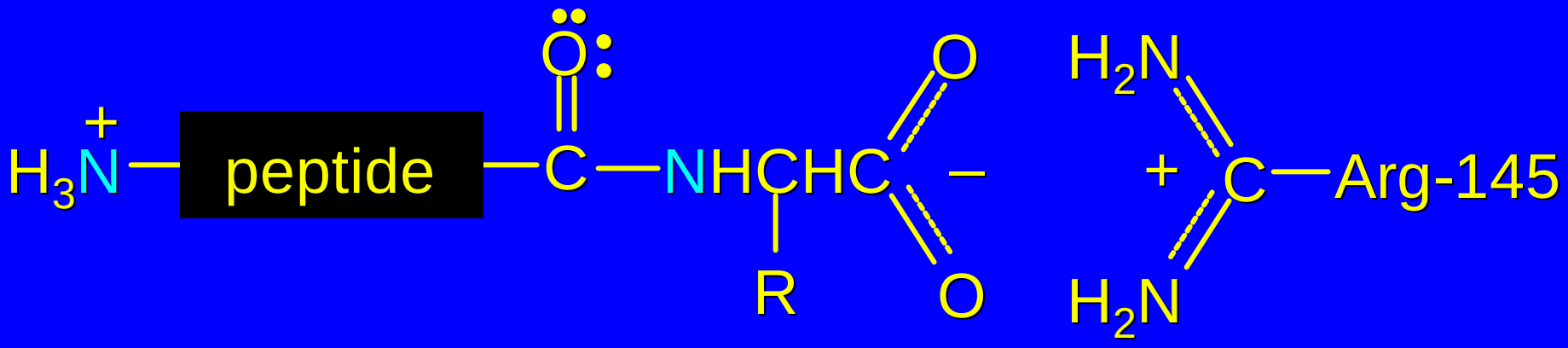
tube model

Disulfide bond

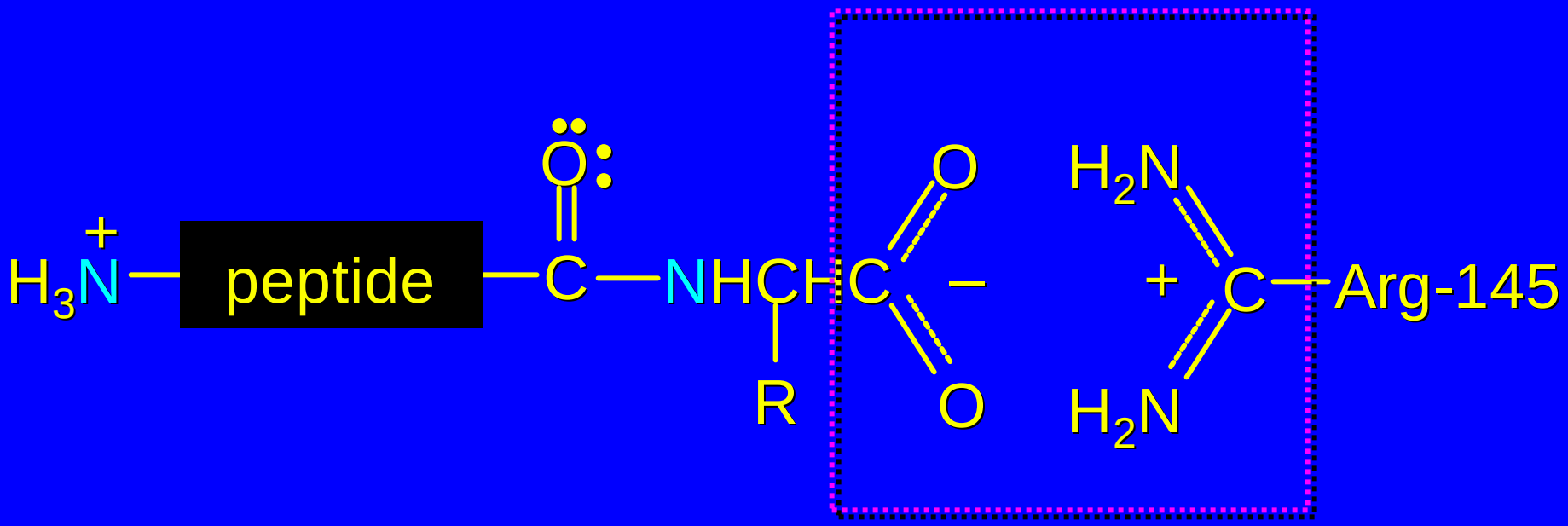


ribbon model

What happens at the active site?

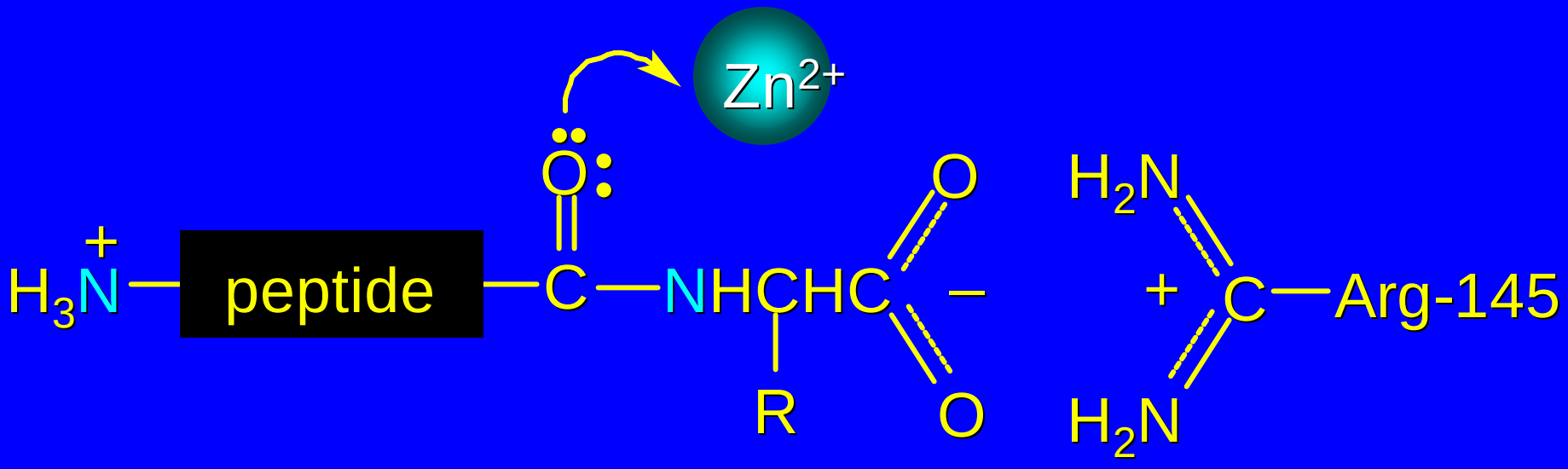


What happens at the active site?



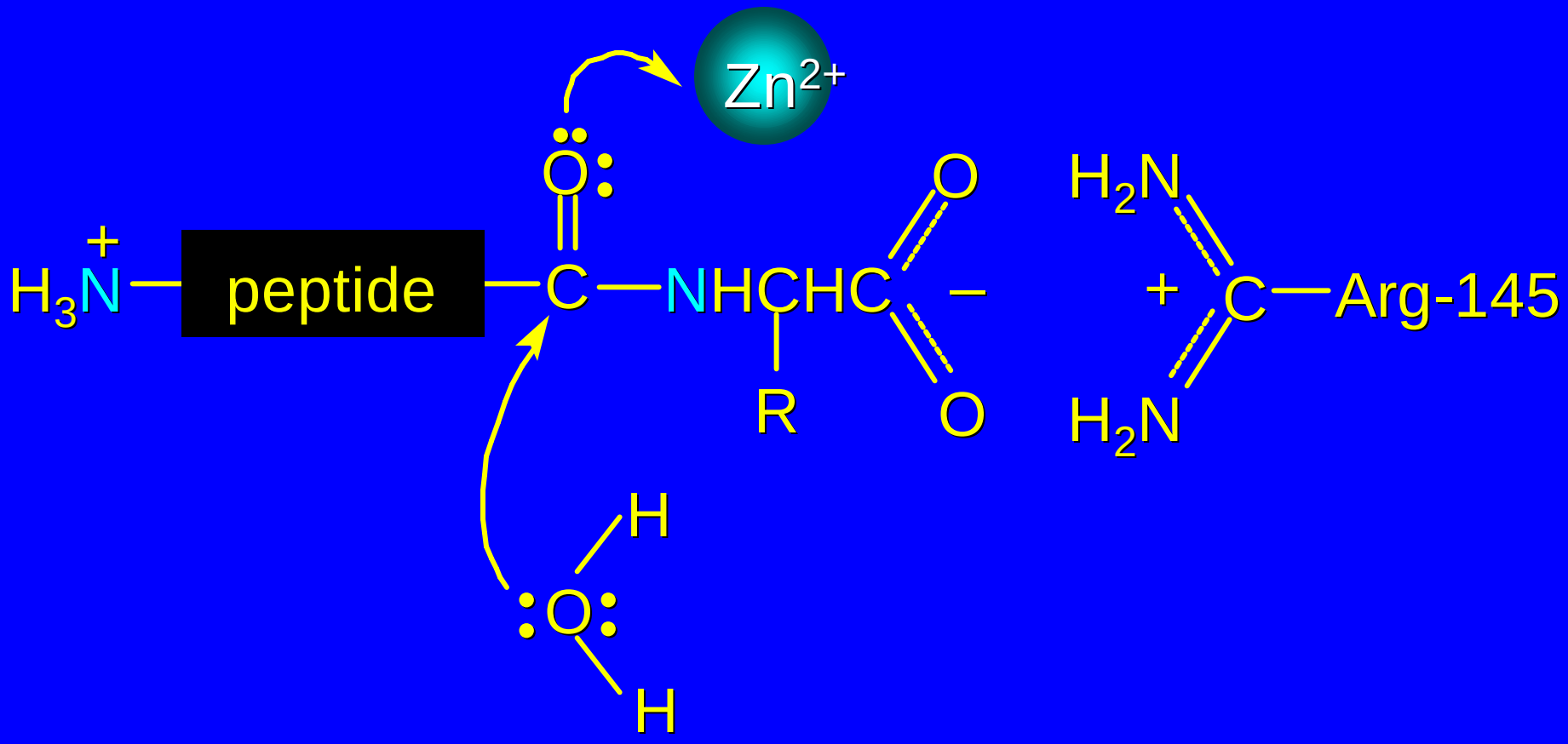
The peptide or protein is bound at the active site by electrostatic attraction between its negatively charged carboxylate ion and arginine-145.

What happens at the active site?



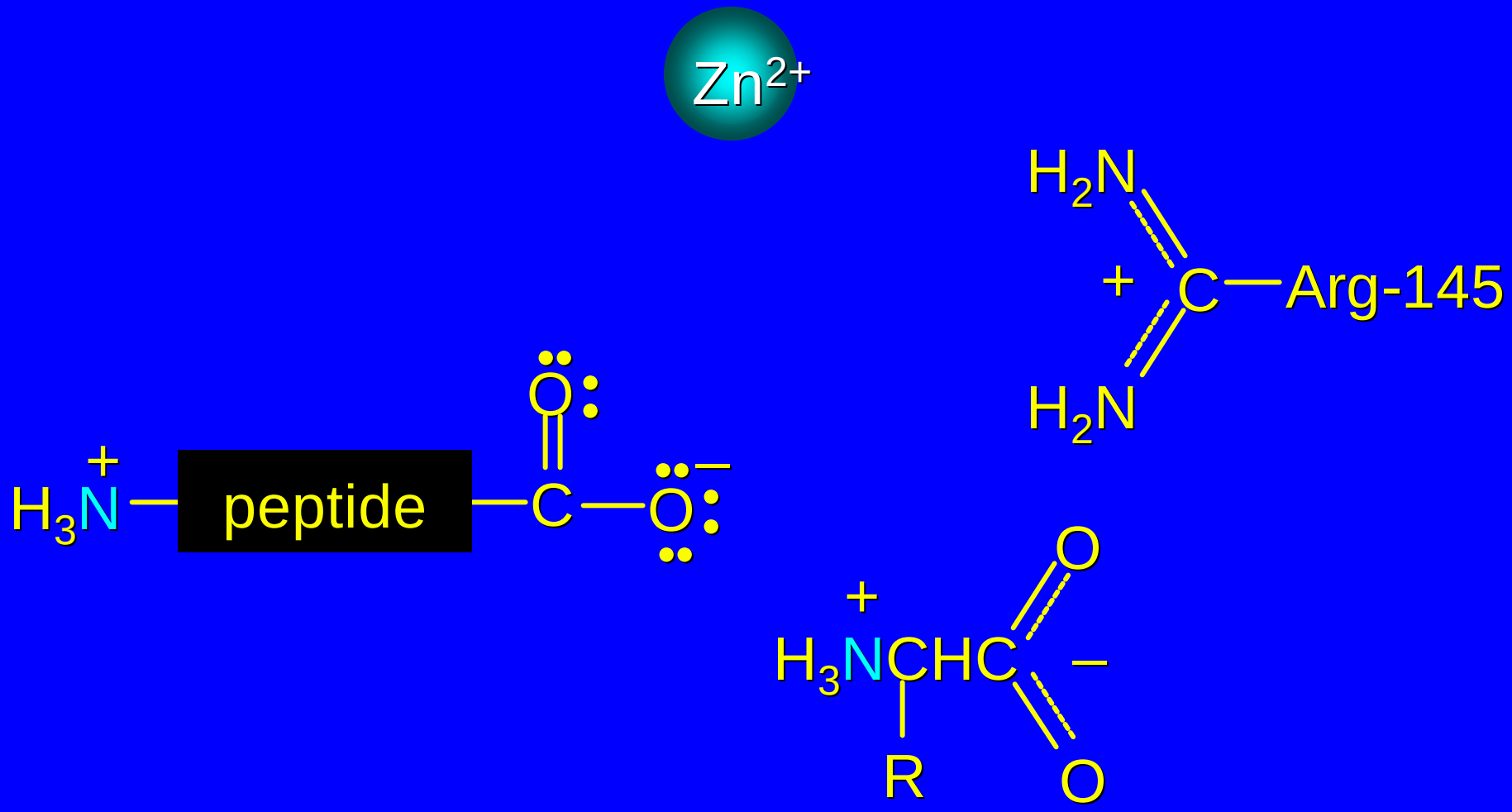
Zn^{2+} acts as a Lewis acid toward the carbonyl oxygen, increasing the positive character of the carbonyl carbon.

What happens at the active site?



Water attacks the carbonyl carbon. Nucleophilic acyl substitution occurs.

What happens at the active site?



27.21
Coenzymes

Coenzymes

The range of chemical reactions that amino acid side chains can participate in is relatively limited.

acid-base (transfer and accept protons)
nucleophilic acyl substitution

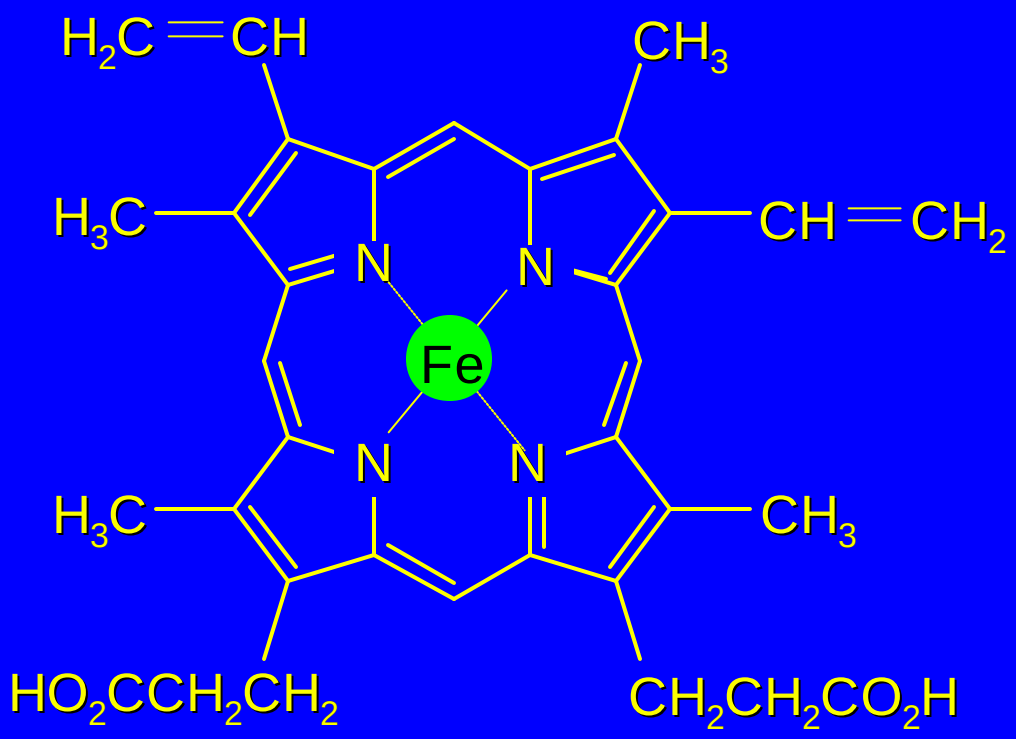
Many other biological processes, such as oxidation-reduction, require coenzymes, cofactors, or prosthetic groups in order to occur.

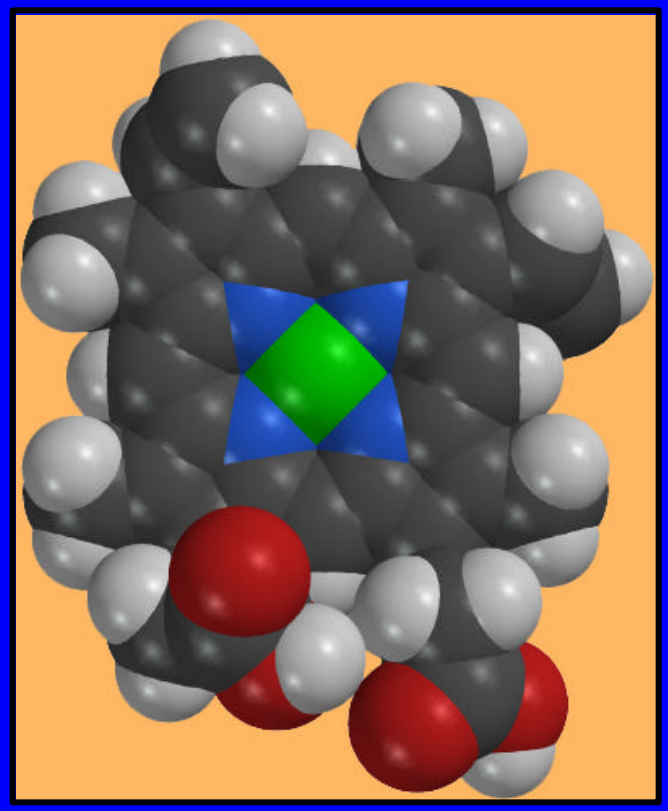
Coenzymes

NADH, coenzyme A and coenzyme B_{12} are examples of coenzymes.

Heme is another example.

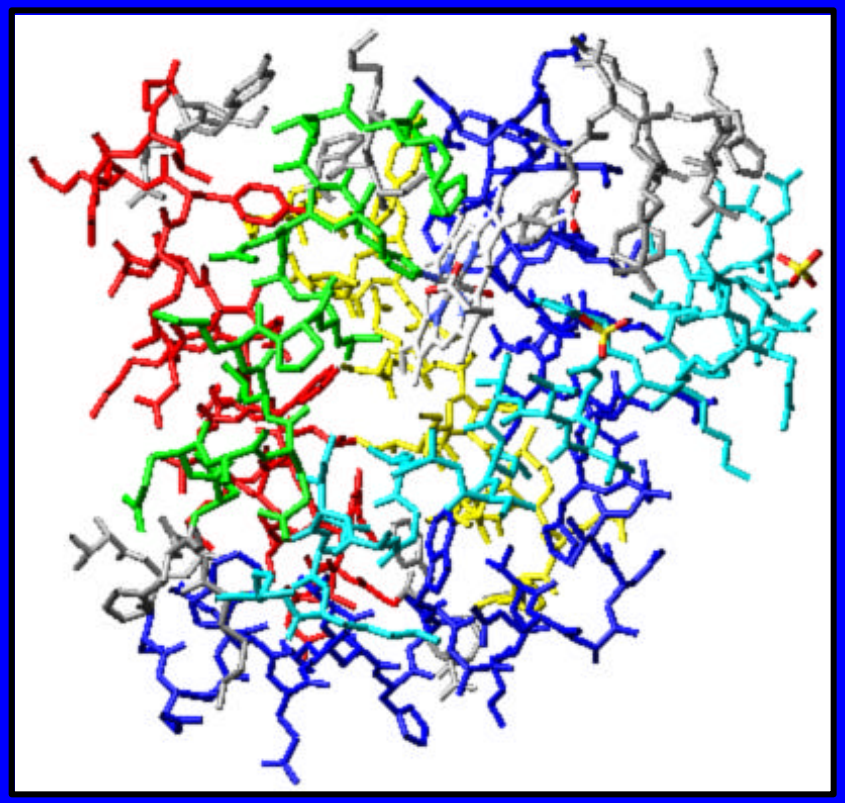
Heme

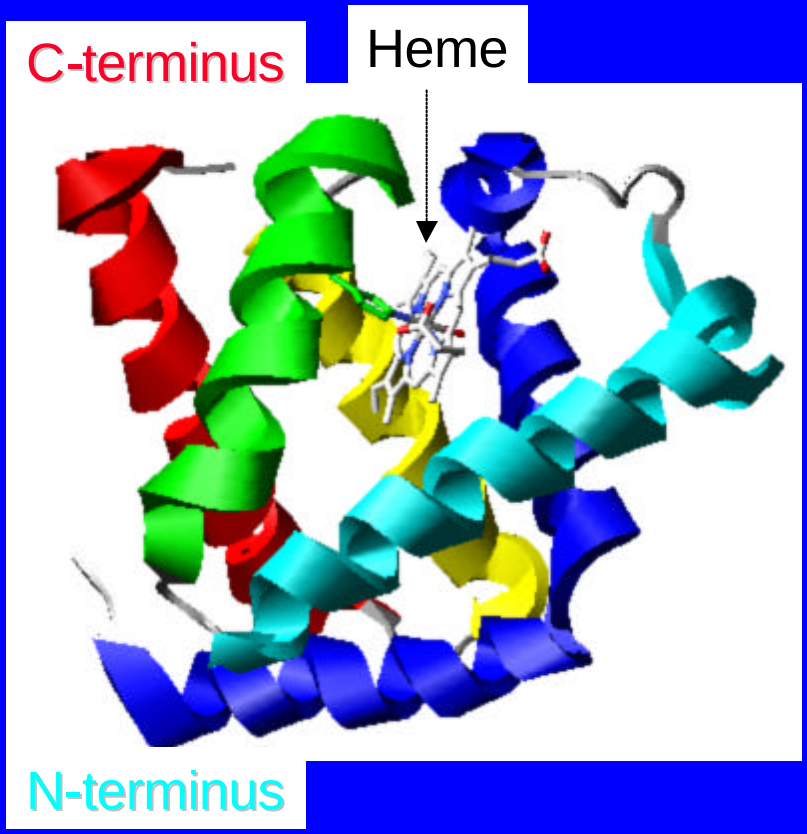




Molecule surrounding iron is a type of porphyrin.

Myoglobin





Heme is the coenzyme that binds oxygen in myoglobin (oxygen storage in muscles) and hemoglobin (oxygen transport).

27.22
Protein Quaternary Structure: Hemoglobin

Protein Quaternary Structure

Some proteins are assemblies of two or more chains. The way in which these chains are organized is called the quaternary structure.

Hemoglobin, for example, consists of 4 subunits.

There are 2 α chains (identical) and 2 β chains (also identical).

Each subunit contains one heme and each protein is about the size of myoglobin.