

On the State of Research into Coordination Compounds of Amino Acids with Metal Ions

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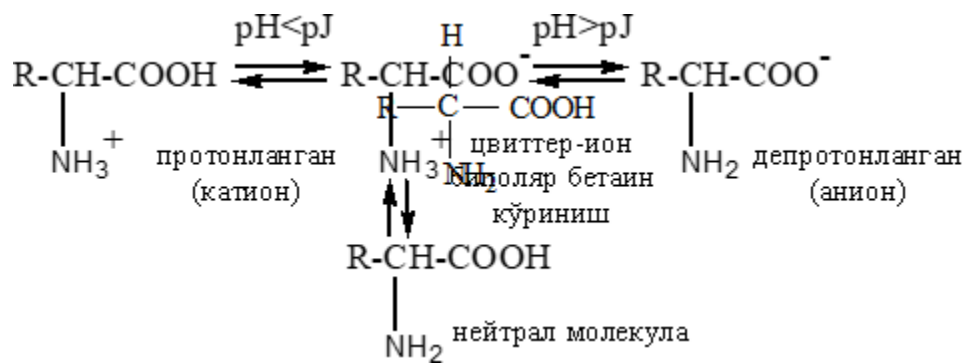
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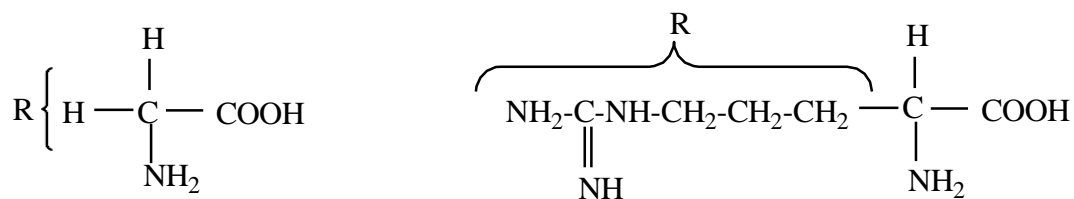
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Annotation: Amino acids are essential substances for the life and activity of humans, animals and plants in nature, they are vital substances for all organisms, being part of proteins, peptides and tissues. Such an important feature of amino acids is due to their chemical composition and physicochemical properties. Among these properties, the amino acid molecule exhibits a neutral molecule, cationic and anionic states in one molecule depending on the environment (pH). In this case, the amino acid molecule polycondenses with its other molecules or with an unlimited number of other amino acid molecules, forming dipeptides, oligo- and polypeptides. This property is to have structures that arise as a result of the connection of peptides, due to their unique composition and the order of formation of proteins that perform various functions in the body.

The acidic properties (pK_a) of amino acids are expressed more strongly in comparison with carboxylic acids, and the basicity properties ($pK_a=9-10$) are more stable in comparison with aliphatic amines. The peculiarity of amino acids is that they simultaneously contain both amino (basic) and carboxyl (acidic) groups, and the molecule is in the α -state in relation to the NH_2 group – the $COOH$ group. At the same time, the NH_2 group is in the ortho-, meta-, para-positions of aromatic amino acids. The diversity of amino acids depends on the composition and structure of the R-side radical, which determines the types of carbon chain and double functional groups and their properties. Natural amino acids are represented by a general formula.

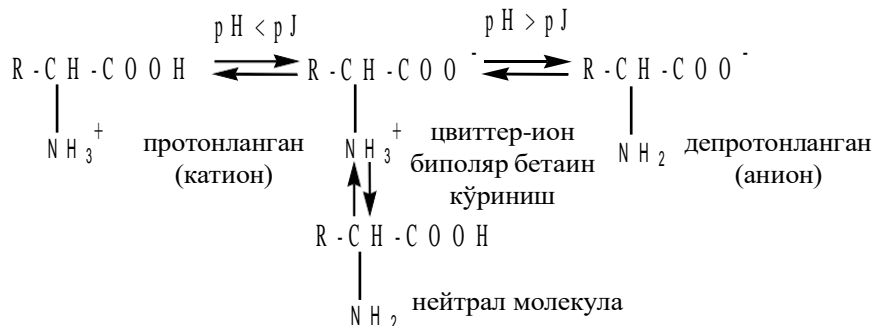


Most amino acids contain one asymmetric carbon atom, so they also exhibit two different optical activities, forming optical isomers. Most naturally occurring amino acids have the L-configuration, with the exception of a number of D-isomeric amino acids. Amino acids differ from each other in the structure (and composition) of R. In its composition, the first representative of the amino acid series can have R=N-atom in glycine or a more complex composition and structure, for example, the structure of the guanidine group in arginine:



Glycine Arginine

Amino acids, when dissolved in water, ionize and exhibit acidic and basic properties due to the NH₂ COOH groups they contain. Organic amphoteric substances – ampholytes containing one amino and one carboxyl group – amino acids crystallize as neutral molecules in which they have a bipolar “betaine” state or “zwitter” – ionic compounds are formed. According to the acid-base balance of the α-amino and carboxyl groups and depending on the solution environment – pH, amino acids are in mutual tautomeric forms [1; P. 200-280].



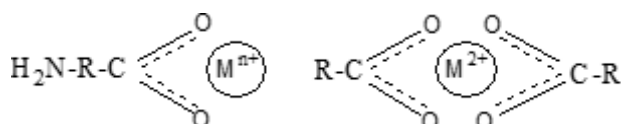
I-isoelectric point, pI-isoelectric indicator, is an indicator of the transition of the amino acid molecule into a zwitterion (betaine form) at the same pH value of the solution. This value is the limiting value of the acid-base property of each amino acid and is one of their main chemical characteristics. As can be seen from the given scheme, the general pH value can be calculated according to Henderson-Hasselbach [1; P. 200-220]. Calculated using the equation ($\text{pH} = \text{pK}_a + \lg \frac{[\text{base}]}{[\text{acid}]}$), its value represents the ratio of equilibrium concentrations [base] ↔ [acid] and the dependence of R on the structure and composition. According to the value of this quantity:

1. The total charge of an amino acid molecule is determined by the solution environment in which they exist - pH, that is, the total charge changes with changes in pH;

2. No two amino acids have exactly the same ionization potential, that is, the pK_a for each amino acid is different.

Therefore, at the same pH, there cannot be two amino acids whose molecules have the same total charge. In addition to the amino and additional carboxyl groups, other functional groups in R also contribute to the total charge of the amino acid molecule. These properties are not only chemical, but also biological. Because the lack of vital components of the body, such as amino acids, vitamins, hormones, enzymes, coenzymes, etc., and in some cases the excess of these substances or the disruption of their metabolism, leads to the emergence and development of various pathological processes.

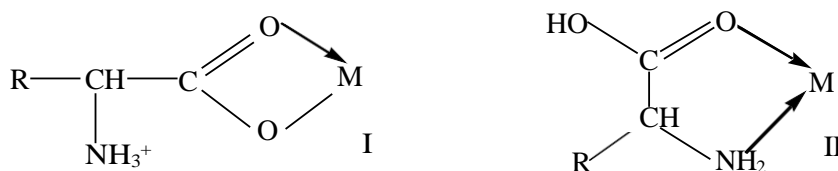
Unshared electron pairs of nitrogen atoms of NH_2 groups and oxygen atoms of $-COOH$ groups in amino acids have the ability to form normal salts and coordination compounds with metal ions (M^{n+}) due to the negative charge caused by the charged electron (O - atom). Usually, during the formation of intermediate salts of amino acids with alkali and alkaline earth metals, electrostatic interaction (ionic bond) occurs with the carboxylate anion of carboxylic acids ($R-COO^-$), forming compounds of the composition $(RCOO)_nM$ ($n=1, 2$). In them, both oxygen atoms in the $-COO^-$ ion are bonded to the carbon atom in the same way, and the negative charge density is uniformly distributed between the O atoms:



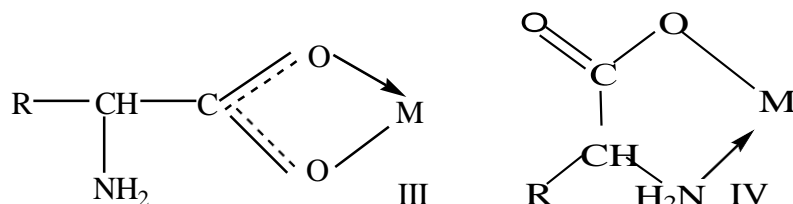
Amino acids, reacting with metal ions with empty p, d, f orbitals in atoms, enter into donor-acceptor interactions through unshared electron pairs of N, O atoms and exhibit the properties of mono-, bi- and polydentate ligands. The products of this interaction are molecular and intramolecular or chelate complex compounds [3; p. 354, 4; p. 25].

Amino acids contain at least 2 functional groups that participate in complex formation with metal ions [M^{n+}]. In the presence of an additional functional group in the side chain, the stability of complex compounds increases due to their participation in M-L bonds [5; pp. 120-156]. The nature and specificity of their ligands in complex formation depend on the pK_d value (K_d is the dissociation constant) of the molecule. The higher the pK_d value, the weaker the ability to bind donor atoms to metal ions.

Amino acids exhibit mono-, bi- and polydentate-ligand properties in complexation reactions depending on the nature of the central ion and the number and nature of functional groups. Amino acids interact with salts of intermediate metal ions in an acidic medium to form molecular complexes (L-amino acid anion, X-acid residue, acido ligand) containing $[ML_nX_m]$ or $[ML_n]X_m$, i.e. fusion products coordinated only through oxygen atoms and form metal rings:



However, the probability of formation of a type II metal ring is lower, since in an acidic environment the amino group is predominantly in the protonated (NH_3^+) state and cannot participate in the formation of the M-L bond [6, pp. 56-80, 7; p. 7]. In a neutral and alkaline environment, the following types of metal rings are formed:



Dibasic amino acids - aspartic and glutamic acids form various complex compounds due to the presence of a second β - and α -COOH group and depending on the location of these groups relative to the amino group. In addition, the replacement of the β - and α -carboxyl group with an amide group (asparagine, glutamine) leads to a change in their coordination ability and identity in the process of complex formation.

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