

COMPLEX COMPOUNDS OF AMINO ACIDS WITH 3D-METALS

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Abstract:

In this work, using modern physicochemical research methods, the interaction of various amino acid solutions with the Cu(II) ion, the structure and properties of the resulting complex compounds were studied. The influence of the environment on the formation of pure and mixed ligand complexes from various obtained amino acids and the constants of stability and instability were determined.

Keywords: *amino acid, 2-aminobutanedicarboxylic acid, thermal analysis, thermal stability, thermolysis, infrared spectroscopy, frequency of symmetric and asymmetric vibrations, stretching vibrations.*

Introduction

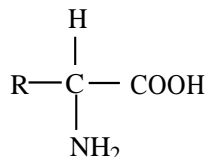
Amino acids are essential substances for the life and activity of humans, animals and plants in nature, are part of proteins, peptides and tissues, and are vital substances for all organisms. Such an important feature of amino acids is due to their chemical composition and physicochemical properties. Among these properties, the amino acid molecule, depending on the environment (pH), exhibits a neutral molecule, cationic and anionic states in one molecule. 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 is the property of forming proteins that perform various tasks in the body, having structures that arise as a result of the combination of peptides due to their specific composition and procedures [1-3].

Carboxyl groups (RCOO⁻) are common ligands and have characteristic structural features in 3d-metal chemistry. Compared to other anionic ligands, alkoxides ($pK_a \geq 16$) or amides ($pK_a \geq 33$), carboxylates (pK_a 1-1-7) exhibit moderate electron-donating properties.

At present, the structure of the studied transition metal carboxylates is very diverse. This is primarily due to the fact that the carboxylate group can be in the form of monodentate and bidentate ligands. In addition, in practice it was found that it exists in the form of a tetradentate ligand. The

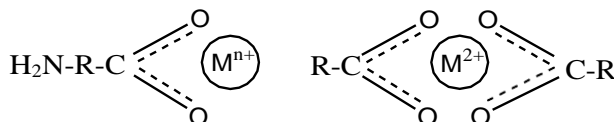
diversity of the structure of carboxylates lies in the electron-donor properties of the oxygen atoms of the carboxyl group, which can form donor-acceptor bonds with several metal atoms simultaneously.

The peculiarity of amino acids is that they contain both amino (basic) and carboxyl (acid) groups, and the NH_2 - group in the molecule is in the α -position relative to the $-\text{COOH}$ group. At the same time, in aromatic amino acids, the NH_2 -group is in the ortho-, meta-, para-positions. 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 the following general formula [4-7].



Most amino acids have one asymmetric carbon atom in their composition, so they also exhibit two different optical activities, forming optical isomers. Most natural amino acids have the L-configuration, and some occur as a series of D-isomer amino acids.

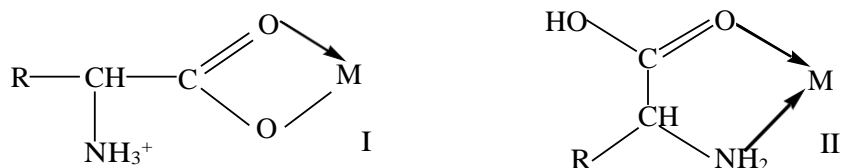
Unshared electron pairs of nitrogen atoms of NH_2 - groups and oxygen atoms of $-\text{COOH}$ groups in amino acids have the ability to form normal salts and coordination compounds with metal ions (M^{n+}) due to the negative charge caused by the charged electron (O - atom). Usually, when forming medium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



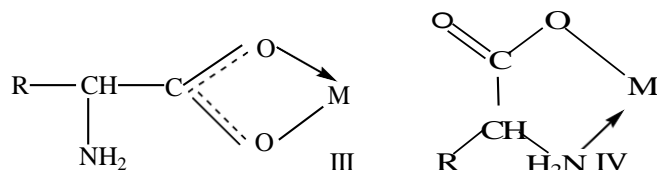
Amino acids, reacting with metal ions with empty p, d, f-orbitals in the atom, enter into donor-acceptor interaction through unshared electron pairs of N, O atoms and exhibit the properties of mono-, bi- and polydentate ligands. As a result of this interaction, molecular and intramolecular or chelate complex compounds are formed [5-8].

Amino acids contain at least 2 functional groups that participate in complex formation with metal ions [M^{n+}]. If there is an additional functional group in the side chain, the stability of complex compounds increases due to their participation in M-L bonds [4, 7]. 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 environment, forming molecular complexes of the composition $[\text{ML}_n\text{X}_m]$ or $[\text{ML}_n]\text{X}_m$ (L-amino acid anion, X-acid residue, acidic ligand), that is, they are coordinated only by oxygen atoms and form metal rings in:



However, the probability of forming a type II metal ring is lower, since in an acidic environment the amino group is predominantly in the protonated state (NH₃⁺) and cannot participate in the formation of the M-L bond [6, 8-10]. 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.

Many types of coordination compounds of natural amino acids with d- and f-elements with ambidentate ligands have been studied [2-4, 10, 11], this [6, 8] contains information on the composition, structure and properties of amino acid complexes of d- and f-elements.

Amino acids are considered "ideal" ligands for studying the processes of complexation of "metals of life" with protein molecules. Since such a pair of substances [M and L] is found in living organisms, it can also be used as a model for the interaction of metals with peptides and proteins [12-14].

The use of cyclodextrin-based complexes (CD) makes it possible to control the mechanisms of drug delivery to the body and radically changes the chemical and pharmacological properties of the original drugs. In the presence of tryptophan and phenylalanine, stable complexes with -CD are formed [14].

The authors of [15] used YaMR spectroscopy to study the interaction processes depending on the concentration of NEM (RZE) ions in an aqueous solution and the pH of the solution. At M:L = 1:2, the carboxyl group coordinates with the metal in exchange for oxygen atoms to form a complex compound.

With a gradual increase in the concentration of metal ions, it was found that a complex compound of the composition M:L = 1:1 is formed in the system and the balance shifts towards the formation of binary complexes.

The zinc ion complex with histidine (R-imidazole, heterocycle) was synthesized and isolated in the solid state; the pH was controlled during the synthesis [10, 13-15]. In the IR spectrum of histidine, NH₂ vibrations are observed in the region of 3400 cm⁻¹, vibrations of the imidazole ring at 1571 cm⁻¹, 1488 cm⁻¹, 1460 cm⁻¹ are due to stretching vibrations of C-N, N-H and the N=C bond, vibrations at 1634 cm⁻¹ indicate that it belongs to the carboxyl group.

Complex compounds of Ni⁺²-ion (3d⁸) were synthesized to study the influence of the paired electron structure when filling 3d-electron orbitals on the composition, structure and properties of complex compounds of amino acids with 3d-metal ions. One of them is a complex with a homo-(Asp)-ligand, and amino acids with radicals R=H, -CH₂-CH₂-COOH and -CH₂-NH-C(NH₂)=NH were

chosen as the second ligand. The coordination of ligands in the complexes and their structure were studied by studying the UV and IR spectra. Electronic absorption spectra of individual aspartic acid and its mixture with second ligands in the UV region in the wavelength range of 200-400 nm were obtained. The absorption maxima observed in the spectra belong predominantly to the $\nu_{C=O}$ group, and their shift confirms the formation of the complex.

To study the coordination sphere of the central ion, electronic absorption spectra of aqueous solutions of nickel (II) sulfate salt and complex compounds were recorded in the range of 400-750 nm in the visible range of light and the results are presented.

In aqueous solutions, the ground state of the nickel (II) ion corresponds to the octahedral coordination state ${}^3A_{2g}(t_{2g})^6(e_g)^2$ [1, 7,9-12]. The Ni (II) ion always has two unpaired electron spins in octahedral coordination. In this case, three electronic transition states are observed: ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F) va ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P). The electronic absorption spectra of the aqueous solution of $NiSO_4$ salt show absorption lines in the regions of $25,000\text{ cm}^{-1}$ (400 nm) and $15,151\text{ cm}^{-1}$ (660 nm), which represent ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) at 400 nm and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ at 660 nm, respectively (F) corresponds to the electronic transition. This shows that the coordination ring of the Ni^{+2} ion in the complex compounds is a partially elongated octahedron. In the spectrum of complex compounds formed by amino acids, the maximum in the region of $25,000\text{ cm}^{-1}$ remains almost unchanged, and the second high-energy part (component) of the absorption line partially changes in the range of $16300\text{-}15150\text{ cm}^{-1}$.

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