

Coordination Chemistry of Copper α - Amino Acid Complexes

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Abstract: This review gives an overview on structures and Coordination chemistry of copper amino acid complexes. A comprehensive review, >120 references, on copper complexes of the amino acids is presented.

Key word: copper, copper complexes, α - amino acid, Coordination chemistry

I. INTRODUCTION

Copper like all metals forms coordination complexes with ligands too. Copper (II) forms stable complexes with amino acids through chelating. Sometimes Copper and amino acids form oxo complexes, which also feature copper(III) [1]. With di- and tripeptides, purple-colored copper(III) complexes are stabilized by the deprotonated amide ligands [2].

Amino acids having both the amine and carboxylic acid groups attached to the first, or alpha, carbon atom have particular importance in biochemistry. They are known as 2-, alpha-, or α -amino acids (generic formula $H_2NCHRCOOH$ in most cases[3][4] where R is an organic substituent known as a "side-chain")[5]; 9 of the 20 standard amino acids are called "essential" amino acids for humans because they cannot be created from other compounds by the human body, and so must be taken in as food. Others may be conditionally essential for some ages or medical conditions. Essential amino acids may also differ between species [6-8].

Copper α amino acid complex attracts attention of chemists because of its different kind of applications. In copper α amino acid complexes syntheses, the amino acid is first reacted with a copper (II) ion and gives a stable square planar copper (II) complex. Subsequently, the copper–amino acid complex is reacted with the amino acid side-chain protecting reagent as the α -amino and α -carboxyl groups are bound to copper (II); the protecting group selectively reacts with the side-chain functional group of a given amino acid. In our previous investigations structures and Coordination chemistry of some copper complexes were reported [9, 10]. In this review an overview on structures and Coordination chemistry of copper amino acid complexes is given. A comprehensive review, >120 references, on copper complexes of the amino acids is presented.

II. COORDINATION CHEMISTRY OF α -AMINO ACID COMPLEXES

II.1. GLYCINE

A new compound $[(Gly)_2Cu][Na(H_2O)_4Cr(OH)_6Mo_6O_{18}] \cdot 9.5H_2O$ (Gly=glycine), has been synthesized. The Compound exhibits an unusual two-dimensional (2D) window-like network constructed from $[Cr(OH)_6Mo_6O_{18}]^{3-}$ as building blocks, Na^+ ions and Cu^{2+} coordination complexes as linkers [11].

A novel compound contains hexanuclear copper cluster and octamolybdate cluster $\{[NaCu_6(Gly)_8(H_2O)_2][Mo_8O_{26}(GlyH)_2(Cu(Gly)H_2O)_2]\} \{NaCu_6(Gly)_8(H_2O)_2\} \{Mo_8O_{26}(GlyH)_2\} \cdot 16H_2O$ has been synthesized. The magnetic measurement of shows that ferromagnetic coupling exists between the magnetic centers of the hexanuclear copper cluster [12]. The decavanadate with a novel glycine–glycinato complex of copper (II) in the cationic part, $(NH_4)_2[Cu_2(H_2O)_4(NH_3CH_2COO)_2(NH_2CH_2COO)_2]H_2V_{10}O_{28} \cdot 6H_2O$, has been prepared. An X-ray structure analysis revealed that the structure contains cationic copper complex with a rare $Cu(H_2O)_2Cu$ double bridge. In this cation, a simultaneous bidentate N, O– and monodentate O– coordination of glycine to the same central atom was observed for the first time [13]. The compound, $[Cu(C_2H_4NO_2)Cl(C_{10}H_8N_2)] \cdot 2H_2O$ reported [14]. And the compound, $[Cu(C_2H_4NO_2)_2(H_2O)]$, reported by Freeman et al [15]. The compound, $trans-[Cu(gly)_2] \cdot 4-BrC_6H_4OH$, when $trans$ -bis(glycinato-N,O)copper(II) and 4-bromophenol were allowed to stand in water for several days are

synthesized. Structural analysis reveals that the 4-bromophenol is not coordinated to the copper and that the glycinate units are trans in N, O-bidentate binding mode. The molecule shows Cu atom in a [4 + 2] coordination mode [16]. A copper(II) coordination polymer with ligation from adenine, glycine, one nitrate anion and a water molecule giving a distorted octahedral coordination geometry with N₃O₃ donor set. Each chain is hydrogen-bonded through C–H···O and N–H···O interactions on both sides leading to an overall polymeric structure [17].

The crystal structure of bisglycino-copper (II) monohydrate was determined. Two glycine molecules are coordinated to the copper (II) ion, forming a planar cis configuration. The irregular octahedral coordination is completed by two oxygen atoms: one belonging to a water molecule and the other a free carboxyl oxygen atom of an adjacent asymmetric unit [18]. Structures of chloro(glycinato)(1,10-phenanthroline)copper(II) monohydrate has been synthesized. The Cu ion displays distorted square-pyramidal coordination with the chlorine atom or the water molecule in the apical position [19]. Structures of aqua(4,7-dimethyl-1,10-phenanthroline)(glycinato)(nitrate)copper(II) monohydrate has been synthesized. The Cu ion displays distorted octahedral coordination [20]. syntheses and structures of chloro(glycinato)(methanol)copper(II) and chloro(glycinato)(1-methylimidazole)copper(II) are reported [21]. The compound [Cu(C₂H₄NO₂)(C₁₆H₁₆N₂)(H₂O)NO₃] has been synthesized. The Cu ion displays distorted square-pyramidal coordination Where the water molecule is in the apical position and the base is defined by the N and one of the O atoms from the glycine ligand, and both phenanthroline N atoms [22]. Coordination polymer and Cu₃(Gly)₄(H₂O)₂(NO₃)₂ was synthesized and characterized structurally. The compound is polymeric chain, consisting from trinuclear blocks Cu₃(Gly)₄(H₂O)₂²⁺. Cu(II) ions are linked by carboxyl-group, while trinuclear units Cu₃(Gly)₄(H₂O)₂²⁺ are linked by NO₃⁻ ions, acting as the bridges between Cu(II) ions of neighboring trinuclear units [23]. The syntheses, structures, and characterization of six Ln³⁺-Cu²⁺-glycine (Hgly) coordination polymers are described [24]. A novel bis(glycinato)copper(II)paradodecatungstate Na₈[{Cu(gly)₂]₂]-{H₂(H₂W₁₂O₄₂)} · 24H₂O has been synthesized under hydrothermal conditions [25]. A novel 3D compound, {K₃H₂[Cu(Gly)₂]₃BW₁₂O₄₀} · 10H₂O (Gly = glycine), has been synthesized. The Compound contains square-grid layers constructed by potassium cations and copper-glycine coordination complexes, the [BW₁₂O₄₀]⁴⁻ anions as templates are accommodated in the square grids by connecting with the K atoms. The K atoms link [BW₁₂O₄₀]⁴⁻ anions from different layers together to yield a 3D novel structure [26]. The copper(II)-glycine-thiocyanate ion system has been studied. The IR spectrum of the solid complex suggests an aquo ligand, a bridging thiocyanato ligand and a N,O-bidentate chelating glycinate ligand. for the complex [Cu(glycinato)(NCS)(H₂O)]_n a tetragonally distorted octahedral structure suggested [27].

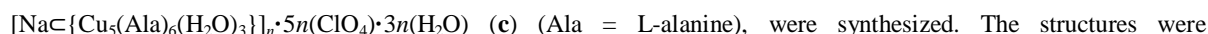
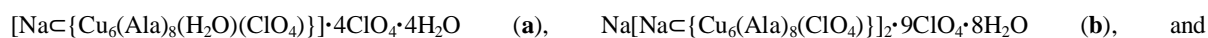
Compound	Coordination number	Ref.
catena-(hexakis(m3-Hydroxo)-decakis(m2-oxo)-tetraaqua-diglycineocta-oxo-chromium-copper-hexamolybdenum-sodium hydrate clathrate)	6	[11]
octakis(m3-Glycinato-N,O,O')-diaqua-hexa-copper(ii)-sodium(i) bis(m4-oxo)-tetrakis(m3-oxo)-hexakis(m2-oxo)-bis(glycine-O)-tetradeca-oxoocta-molybdenum(vi) tetrakis(m4-oxo)-octakis(m3-glycinato-N,O,O')-octakis(m3-oxo)-bis(m2-glycine-O,O')-hexadecakis(m2-oxo)-tetra-aquabis(glycine-N,O)-bis(glycine-O)-tetracosa-oxo-octa-copper(ii)-hexadecamolybdenum(vi)-sodium(i) heptadecahydrate	5	[12]
diammonium bis(m2-aqua)-tetraaqua-bis(glycinato)-bis(glycine)-dicopper(ii) bis(m6-oxo)-bis(m3-hydroxo)-bis(m3-oxo)-tetradecakis(m2-oxo)-octa-oxo-tetra-vanadium hexahydrate	6	[13]
(2,2'-Bipyridyl-k2N,N')-chloro-(glycinato-k2N,O)-copper(ii) dihydrate	5	[14]
cis-Aqua-bis(glycinato-N,O)-copper(ii)	5	[15]
catena-(trans-bis(Glycinato-N,O)-copper(ii)4- bromophenol solvate)	5	[16]
catena-[(m2-Adenine)-aqua-(glycinato-N,O)-nitrate-copper(ii)]	6	[17]
cis-bis(Glycinato-N,O)-copper(ii) monohydrate	4	[18]
Chloro-(glycinato-N,O)-(1,10-phenanthroline-N,N')-copper(ii) monohydrate	5	[19]
Aqua-glycinato-(4,7-dimethyl-1,10-phenanthroline)-nitrate-copper(ii) monohydrate	6	[20]
catena-(m2-Chloro-(glycinato-N,O,O')-(1-methylimidazole-N)-copper(ii))	5	[21]
Aqua-(glycinato-N,O)-(3,4,7,8-tetramethyl-1,10-phenanthroline)-copper(ii) nitrate	5	[22]
catena-(bis(m2-Glycinato)-bis(m2-nitrate-O,O')-diaqua-bis(glycinato-N,O) -tri-copper(ii))		[23]
catena-(Di-sodium (m10-perchlorato)-decakis(m3-glycinato)-octacosakis(m3-hydroxo)-tetrakis(m2-2-ammonioacetato)-bis(m2-glycinato)-hexakis(m2-glycinato)-tetradeca-aqua-hexa-europiumpentacosacopper tricosaperchlorate hydrate)		[24]
catena-(Octa-sodium bis(m3-hydroxo)-tetrakis(m3-oxo)-bis(m2-hydroxo)-icosakis(m2-oxo)-tetradeca-oxo-tetrakis(glycine-N,O)-di-copper(ii)-dodeca-tungsten hydrate)	6	[25]
catena-((m12-tetraoxoborato)-bis(m3-glycinato)-bis(m3-oxo)-tris(m2-glycinato)-bis(m2-hydroxo)-(m2-aqua)-pentacontakis(m2-oxo)-penta-aqua-(glycinato)-hepta-oxo-tri-copper-tri-potassium-dodecatungstentetrahydrate)	4	[26]

Catena-(Glycinato-aqua-(m2-thiocyanato)-copper(ii))	5	[27]
N, N'-Bipyridyl-glycinato-chloro-copper (ii) dihydrate	5	[28]
(2, 2'-Bipyridyl-N, N')-chloro-(glycinato-N, O)-copper (ii) dihydrate	5	[29]
Sodium aqua-(glycinato-N, O)-(orotato-N, O)-copper trihydrate	5	[30]
cis-bis(Glycinato-N,O)-copper(ii) monohydrate	4	[31]
Copper (ii) glycinate monohydrate	4	[32]
cis-Aqua-bis(glycinato-N,O)-copper(ii)	5	[33]
Aqua-(L-glycinato-N,O)-(1,10-phenanthroline)-copper(ii) nitrate sesquihydrate	5	[34]
Diammonium bis((2-aminoacetato-k2N,O)-(2,2'-bipyridine-k2N,N')-(N,NNdimethylformamide-kO)-copper(ii)) bis(m5-oxo)-tetrakis(m3-oxo)- hexakis(m2-oxo)-tetradecakis(oxo)-octa-molybdenum(vi)	5	[35]
cis,cis-(1,3,5-Triaminocyclohexane)-(glycinato)-copper(ii)tetraphenylborate	5	[36]
(cis,cis-1,3,5-Triaminocyclohexane-N,N',N'')-(glycinato-N,O)-copper(ii) tetraphenylborate	5	[37]
(m2-Dipicolinamideazino)-bis(glycyl)-aqua-nitrato-di-copper(ii) nitrate monohydrate	5	[38]
catena-((m10-Perchlorato)-decakis(m3-glycinato)-octacosakis(m3-hydroxo)-tetrakis(m2-2-ammonioacetato)-bis(m2-glycinato)-hexakis(m2-glycinato)-hexadeca-aqua-hexa-bis(perchlorato-O)-dysprosiumpentacosa-copper nondecaperchlorate docosahydrate)		[39]
Catena-((m2-glycinato-N, O, O')-aqua-copper (ii) perchlorate)	4	[40]
Catena-(Aqua-(m2-glycinato-N, O, O')-(nitrato-O)-copper (ii))	5	[41]
Glycinato-L-serinato-copper (ii)	4	[42]
Aqua-(dipyrido[3,2-a:2',3'-c]phenazine)-(glycinato)-copper(ii) nitrate monohydrate	5	[43]
catena-(Sodium hexa-aqua-sodium bis(glycinato)-copper heptahydriddodecatungstate-tris(tetra-aqua-sodium) hydrate)	4	[44]
Chloro-(glycinato-N, O)-(1,10-phenanthroline-N,N')-copper(ii) trihydrate	5	[45]
D, L-Serinato-glycyl-copper (ii)	4	[46]
Glycinato-(D, L-serinato)-copper (ii)	4	[47]
Disodium octakis(m2-glycinato)-diaqua-hexa-copper hexaperchlorate dihydrate	4	[48]
Sodium (glycinato-N,O)-(N-(4-methylphenylsulfonyl)glycinato-N,O)-copper(ii) dihydrate	4	[49]
Chloro-(glycinato-N,O)-(bis(2-pyridyl)amine-N,N')-copper(ii) monohydrate	5	[50]
Chloro-(glycinato-N, O)-(1, 10-phenanthroline-N, N')-copper (ii) hydrate	5	[51]
Aqua-(glycinato-N,O)-(1,10-phenanthroline-N,N')-copper(ii) perchlorate hydrate	5	[52]
Diammonium octa-sodium bis(m3-hydroxo)-tetrakis(m3-oxo)- octadecakis(m2-oxo)-octadeca-oxo-dodeca-tungsten henicosa-hydrate	4	[53]
catena-(hexakis(m3-Hydroxo)-tetrakis(m2-aqua)-bis(m2-glycinato)-decakis(m2-oxo)-hexa-aqua-octa-oxo-copper(ii)-chromium-examolybdenum(vi)-tri-sodium trihydrate)	6	[54]
Trioxonium tri-sodium (m2-dihydropolyoxododecatungstate)-bis(cisbis(glycinato)-copper(ii)) hydrate	5	[55]
cis-bis(glycinato)-aqua-copper(ii)	5	[56]

II.2. ALANINE

Structure of *trans*-bis(DL- α -alaninato)copper(II) monohydrate [57] and The crystal structure of the copper complex of L-alanine has been synthesized [58]. The complex of L-alaninato(aqua)(4,7-diphenyl-1,10-phenanthroline)copper(II) nitrite monohydrate reported. The Cu ion displays square-pyramidal coordination with an apical water molecule [59]. Crystal structure and magnetic interactions in bis(D,L-alaninato)copper(II) hydrate reported [60]. The complex of $\{[\text{Cu}_2(\text{L-alaninato})_2(4,4'\text{-bipy})_2(\text{H}_2\text{O})_2]_2[\text{NO}_3]_4 \cdot 6\text{H}_2\text{O}\}_n$ (4,4'-bipy = 4,4'-bipyridine), was synthesized through self-assembly of Cu(II)-amino acid five-membered rings and 4,4'-bipy [61]. Four new ternary copper(II) complexes of α -amino acid having polypyridyl bases of general formulation $[\text{Cu}(\text{L-ala})(\text{B})(\text{H}_2\text{O})](\text{X})$, where L-ala is L-alanine, B is an N,N-donor heterocyclic base, viz. 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen,) and 5,6-phenanthroline dione (dione), dipyrido[3,2:2',3'-f]quinoxaline (dpq), and $\text{X} = \text{ClO}_4^- / \text{NO}_3^-$ are synthesized. The complexes show a distorted square-pyramidal (4 + 1) CuN_3O_2 coordination geometry [62]. The structure of *cis*-bis(L-alaninato)copper(II) $\{cis\text{-}[\text{Cu}(\text{L-ala})_2]\}$ was determined. The alanine ligands coordinate to the divalent copper atom in an approximately square planar *cis*-arrangement [63]. The new copper(II) complexes of formulae $[\text{Cu}(\mu\text{-ala})(\text{im})(\text{H}_2\text{O})]_n(\text{ClO}_4)_n$, $[\text{Cu}(\mu\text{-ala})(\text{pz})(\mu\text{-ClO}_4)]_n$ have been characterized (ala = alanine; im = imidazole; pz = pyrazole). In all cases, the deprotonated amino acid ligand acts as chelate through the N(amine) and one O(carboxylato), whereas the second O atom of the same carboxylato acts as a bridge to the neighbouring copper(II) ion [64]. Thiocyanato-Cu (II) complexes including polymeric 1D $[\text{Cu}(\text{D,L-Ala})(\mu_{\text{N,S}}\text{-NCS})(\text{H}_2\text{O})]_n$ was synthesized (Ala = alaninate anion). The complex forms a 1-D polymeric chain with the NCS^- acting as a $\mu_{\text{N,S}}$ -ligand. A distorted square-pyramidal geometry around the Cu^{2+} centers was achieved by the O and N atoms of alaninato anion, the aqua ligand and by the N and S atoms of the bridging thiocyanate groups. Hydrogen bonds of the type $\text{N-H}\cdots\text{O}$, $\text{N-H}\cdots\text{S}$ and $\text{O-H}\cdots\text{O}$ are formed in this complex leading to the extension of the 1D chain to a supramolecular network [65]. The crystal and molecular structures of the *trans*

complexes [Cu(DL-alaO)₂(H₂O)], [Cu(L-alaO)₂] [alaO = alaninate(1-)] are reported. The single-crystal e.s.r. spectrum of *cis*-[Cu(glyO)₂(H₂O)] [glyO = glycinate(1-)] was also measured, and the small in-plane anisotropy of the molecular *g* tensor confirmed the interpretation of the *g* values of the *trans* amino acid complexes. Angular overlap calculations of the *d-d* transition energies and molecular *g* values of the complexes suggest metal–ligand bonding parameters consistent with their molecular structures. However, in agreement with similar findings on analogous compounds the *d_z²→d_{x²-y²}* transitions were found to lie at anomalously high energy, this discrepancy being most marked when the axial bonds are very long [66]. three sodium-centered polynuclear octahedral copper(II)–amino acid clusters,



characterized by X-ray structure analysis. The structure of **a** can be described as an octahedron formed with six copper atoms in which four Cu(Ala)₂ ligands bridge two axial copper ions and capture one Na⁺ in the center of the cage and that of **b** as an octahedral dimer that is linked by two carboxylate oxygen atoms. Complex **c** is a chain composed of incomplete octahedron [NaCu₅] units linked together by two carboxylate oxygen atoms. The magnetic susceptibility measurements indicate that all three clusters are ferromagnetic [67]. The crystal and molecular structure of a new crystalline modification of bis-[D-alaninato] copper (II), Cu (C₃H₆NO₂)₂' has been determined. The inner co-ordination sphere around the copper atom is square pyramidal; the two bidentate α-amino acid rings are *cis* and form the basal plane of the pyramid, the apex being occupied by a carboxylate oxygen atom, from a neighbouring molecule, at a distance of 2.390(7)Å [68].

Compound	Coordination number	Ref.
trans-bis(DL-a-Alaninato-N,O)-copper(ii) monohydrate	4	[57]
trans-bis(L-a-Alaninato)-copper(ii)	4	[58]
L-Alaninato-aqua-(4,7-diphenyl-1,10-phenanthroline)-copper(ii) nitrite monohydrate	5	[59]
bis(D,L-Alaninato-O,N)-copper(ii) monohydrate	4	[60]
catena-(bis((m2-4,4'-bipyridyl)-(L-alaninato)-aqua-copper(ii) nitrate) trihydrate)	5	[61]
(L-Alaninato)-(aqua)-(1,10-phenanthroline)-copper nitrate hydrate and (Alaninato)-(aqua)-(1,10-phenanthroline-5,6-dione)-copper nitrate	5	[62]
catena-(cis-(m2-L-Alaninato)-(L-alaninato)-copper(ii))	5	[63]
catena-((m2-Alaninato)-aqua-(imidazole)-copper(ii) perchlorate) and catena-((m2-Alaninato)-(m2-perchlorato)-(pyrazole)-copper(ii)) and catena-((m2-Phenylalaninato)-aqua-(imidazole)-copper(ii) perchlorate)	5 6 5	[64]
catena-[(m2-Thiocyanato-N,S)-(D,L-alaninato-N,O)-aqua-copper(ii)]	5	[65]
trans-bis(L-Alaninato-N,O)-copper(ii)	4	[66]
octakis(m3-Alaninato)-aqua-(perchlorato-O)-hexa-copper(ii)-sodium tetraperchlorate trihydrate	5	[67]
catena-(cis-bis(D-Alaninato)-copper(ii))	5	[68]
catena(L-Alaninato-aqua-L-histidinato-copper(ii) trihydrate	5	[69]
Aqua-(L-proline-L-alanine)-copper(ii) sesquihydrate	4	[70]
trans-bis(L-Alaninato-N,O)-copper(ii)	4	[71]
trans-bis(D,L-Alaninato-N,O)-copper(ii) monohydrate	4	[72]
catena-(m2-Aqua)-bis(DL-alaninato-N,O)-copper(ii)	6	[73]
(m2-Dipicolinamideazino)-bis(alanyl)-diaqua-di-copper(ii) dinitrate trihydrate	5	[74]
catena-(bis(m2-4,4'-bipyridine-N,N')-(D-alaninato)-(L-alaninato)-diaqua-dicopper(ii) bis(nitrate) trihydrate	5	[75]
catena-(m2-L-Alaninato)-(2,2'-bipyridyl)-copper(ii) perchlorate monohydrate)	5	[76]
bis(m4-Alaninato)-tetradecakis(m3-alaninato)-(m2-perchlorato-O,O')-tetra-aqua-bis(perchlorato-O)-dodeca-copper(ii)-tri-sodiumoctaperchlorate tetrahydrate		[77]
catena-(bis(m4-Alaninato-N,O,O,O')-tetrakis(m3-alaninato-N,O,O,O')-triacqua-penta-copper(ii)-sodium pentaperchlorate trihydrate)		[78]
catena-(m2-L-Alaninato)-(1,10-phenanthroline)-copper(ii) perchlorate monohydrate)	5	[79]

II.3. ARGININE

Copper(II) complexes $[\text{Cu}(\text{L-arg})_2](\text{NO}_3)_2$ (**1**) and $[\text{Cu}(\text{L-arg})(\text{B})\text{Cl}]\text{Cl}$ (**2–5**), where B is a heterocyclic base, namely, 2,2'-bipyridine (bpy, **2**), 1,10-phenanthroline (phen, **3**), dipyrrodo[3,2-d:2',3'-f]quinoxaline (dpq, **4**), and dipyrrodo[3,2-a:2',3'-c]phenazine (dppz, **5**), are prepared. Ternary complex **3**, structurally characterized using X-ray crystallography, shows a square-pyramidal (4 + 1) coordination geometry in which the N,O-donor L-arginine and N,N-donor 1,10-phenanthroline form the basal plane with one chloride at the elongated axial site. The one-electron paramagnetic complexes display a metal-centered d-d band in the range of 590–690 nm in aqueous DMF [80].

Ternary copper(II) complexes containing an acidic amino acid (A) and a basic amino acid (B), Cu(A)(B), where A refers to ethylenediamine-N-monoacetic acid (EDMA) and DL-diaminopropionic acid (DAP) and B to L-arginine and L-lysine, have been investigated. The Cu ion is in a slightly distorted square-pyramidal geometry. With the two nitrogen atoms of EDMA and the nitrogen and oxygen atoms of L-Arg coordinated at the equatorial positions and the carboxylate oxygen atom of EDMA coordinated at an axial position. A perchlorate oxygen atom weakly coordinates at the other axial site [81]. The crystal structures of $[\text{Cu}(\text{L-Arg})_2]^{2+}\text{X}^{2-}$ systems, where X refers to dinegative tetrahedral anions, sulfate or 1,3-benzenedisulfonate (*m*-bs²⁻) studied. The molecular structure of $[\text{Cu}(\text{L-Arg})_2](\text{SO}_4)$ exhibited a planar Cu(II) geometry with the two coordinated amino groups in the *cis* configuration due to the hydrogen bonds with SO_4^{2-} , and the complex with $\text{X}^{2-}=\text{m-bs}^{2-}$ assumed the *trans* configuration without hydrogen bonds with *m-bs*²⁻ [82]. The crystal structure of bis(L-arginine)Cu(II)(acetate)₂ trihydrate has been determined by X-ray analysis. Each copper atom has an essentially square planar coordination with the two arginine molecules chelated via the carboxy oxygens and the α -amino nitrogens, but with distorted six-fold coordinations completed by weak Cu...O (acetate) interactions. Electrostatic interactions between the acetates and the protonated ends of the amino acid residues link the two independent $[\text{Cu}(\text{L-arginine})_2(\text{acetate})_2]$ units into dimers, which are then connected via hydrogen bonds, also involving the water molecules, into an infinite network [83]. The $[\text{Cu}(\text{L-Arg})_2]^{2+}$ complex ions (Arg=arginine) in the presence of aromatic carboxylates has been studied by spectroscopic and X-ray diffraction methods. $[\text{Cu}(\text{L-Arg})_2]\text{Cl}_2$ dissolved in aqueous solutions containing benzene-1,4-dicarboxylate (terephthalate, *p*-pa²⁻) and -1,2,4,5-tetracarboxylate (pyromellitate, pma⁴⁻) gave crystals of $[\text{Cu}(\text{L-Arg})_2](\text{p-pa}) \cdot 2\text{H}_2\text{O}$ and $[\text{Cu}(\text{L-Arg})_2](\text{pma}) \cdot 4\text{H}_2\text{O}$ respectively. Both complexes have a square-planar structure with two L-Arg molecules in the *trans* configuration [84]. The synthesis, characterization and crystal structure of a novel dinuclear copper compound with L-arginine, mono and bidentate HPO_4^{2-} oxoanions and an OH⁻ anion $[\text{Cu}_2(\text{L-arg})_2(\mu\text{-HPO}_4\text{-O})(\mu\text{-HPO}_4\text{-O,O})(\mu\text{-OH})] \cdot (\text{H}_3\text{O})^+ \cdot 6\text{H}_2\text{O}$ are reported. The two independent copper ions are in a distorted square pyramidal coordination, each bonded to one L-arginine molecule [85]. Complexes of the type $[\text{Cu}(\text{Arg})_2](\text{L}) \cdot n\text{H}_2\text{O}$ (L = aromatic dicarboxylate, *n* = 5,6) formed by self-assembly show double-helical structures in the solid state, which comprise infinite $[\text{Cu}(\text{Arg})_2]^{2+}\text{-L}^{2-}$ strands [86].

Compound	Coordination number	Ref.
(L-Arginine-N,O)-chloro-(1,10-phenanthroline)-copper(ii) chloride hydrate	5	[80]
(L-Arginine)-(ethylenediamine-N-monoacetic acid)-copper(ii) perchlorate ethanol solvate and bis(L-Arginine)-copper(ii) dinitrate trihydrate	5 4	[81]
Aqua-bis(L-arginine-N,O)-copper(ii) m-phthalate pentahydrate and Aqua-bis(L-arginine-N,O)-copper(ii) 2,6-dipicolinate tetrahydrate and Aqua-bis(D-arginine-N,O)-copper(ii) 3,5-dipicolinate tetrahydrate	5	[82]
(Acetic acid-O)-bis(L-arginine-N,O)-copper(ii) acetic acid trihydrate	5	[83]
bis(L-Arginine-N,O)-copper(ii) terephthalate dihydrate	4	[84]
Oxonium (m2-hydrogen phosphato-O,O')-(m2-hydrogen phosphato-O,O)-(m2-hydroxo)-bis(L-arginine-N,O)-di-copper(ii) hexahydrate	5	[85]
Aqua-bis(L-arginine-O,N)-copper(ii) (m-phthalate) pentahydrate	5	[86]
catena-[bis(m2-Perchlorato)-bis(L-arginine)-bis(2,2'-bipyridyl)-dicopper(ii) diperchlorate tetrahydrate	6	[87]
trans-bis(L-Arginine-N,O)-(nitrate-O)-copper(ii) nitrate trihydrate	5	[88]
catena-(cis-(m2-L-Arginine-N,O,O')-(L-arginine-N,O)-copper(ii) dinitratetrihydrate)	5	[89]
Aqua-bis(D-arginine-N,O)-copper(ii) m-phthalate pentahydrate and Aqua-bis(L-arginine-N,O)-copper(ii) sulfate pentahydrate and bis(L-Arginine-N,O)-copper(ii) 1,3-benzenedisulfonate	5 4	[90]
Aqua-bis(L-arginine-O,N)-copper(ii) (2,6-dipicolinate) tetrahydrate and Aqua-bis(D-arginine-O,N)-copper(ii) (3,5-dipicolinate) tetrahydrate	5	[91]

II.4. TRYPTOPHANE

The ternary copper (II) complex of 6-deoxy-6-[(2-(4-imidazolyl) ethyl) amino]cyclomaltoheptaose (CDhm) and L-tryptophanate (L-TrpO⁻) was performed. The solid state structure of [Cu(CDhm)(L-TrpO)]⁺ shows that the aromatic side chain of TrpO⁻ is outside the cavity and that the two amino nitrogen atoms, one from the histamine molecule and one from the amino acidate, are in a cis disposition. The two amino nitrogens, the imidazole nitrogen, and the carboxylate oxygen atoms form the base of a square pyramid, which surrounds the copper (II) ion, a water molecule occupying an apical position. Atomic distances suggest for this complex that π - π and d- π interactions could occur in the solid state [92]. The ternary copper (II) complex of [Cu(bpy)(L-trp)]ClO₄ and [Cu(phen)(L-trp)]ClO₄ have been investigated. The Cu(II) ion is five-coordinate square-pyramidal, with the two nitrogen atoms of bpy and the nitrogen and oxygen atoms of the amino acid coordinated at the equatorial positions in a slightly distorted square-planar form and the carboxylate oxygen atom of the neighboring molecule at the axial position. The absorption bands due to the charge transfer (CT) interaction between the indole ring and the aromatic diamine have been observed in the difference spectra in the near ultraviolet region [93]. The ternary copper(II) complex of [Cu(L-trp)(B)(H₂O)](NO₃) (B: phenanthroline bases, L-trp: L-tryptophan) has been synthesized and show the presence of a square pyramidal (4 + 1) CuN₃O₂ coordination geometry in which the N,O-donor amino acid (L-trp) and N,N-donor phenanthroline base bind at the equatorial plane with an aqua ligand coordinated at the elongated axial site [94]. Ternary Cu(II) complexes containing an aromatic diimine (DA = di(2-pyridylmethyl)amine (dpa), 4,4'-disubstituted 2,2'-bipyridine (Y₂bpy; Y = H (bpy), Me, Cl, N(Et)₂, CONH₂ or COOEt) or 2,2'-bipyrimidine) and an aromatic amino acid (AA = L-phenylalanine (Phe), *p*-substituted phenylalanine (XPhe; X = NH₂, NO₂, F, Cl or Br), L-tyrosine (Tyr), L-tryptophan (Trp) or L-alanine (Ala)) were characterized by X-ray diffraction. The structure of [Cu(dpa)(Trp)]ClO₄·2H₂O in the solid state was revealed to have intramolecular π - π interactions between the Cu(II)-coordinated aromatic ring moiety, Cu(DA) (M π), and the side chain aromatic ring of the AA (L π) [95]. The ternary copper (II) complexes [Cu(L-trp)(bpy)](ClO₄) and [Cu(L-trp)(phen)](ClO₄)·3H₂O (where L-trp = L-tryptophan, bpy = bipyridyl, phen = phenanthroline) have been synthesized [96]. The two-dimensional mixed-ligand network catena-[(μ -4, 4'-bipyridine)-bis(μ -L-tryptophanato- κ^3 N, O, O')-diaqua-dicopper (II) dinitrate] is constructed through the bridging action of both the tridentate amino carboxylate and the bidentate 4,4'-bipyridine ligand. The enantiomeric L-tryptophanato ligand acts as an *N,O* chelate towards one copper atom and bridges through the second carboxylate oxygen atom to the adjacent copper ion [97].

Compound		Coordination number	Ref.
Aqua-(6-deoxy-6-N-histamino-b-cyclodextrin-N,N')-(L-tryptophan-N,O)-copper(ii) tetradecahydrate	nitrate	5	[92]
catena-((PP)-(m2-L-tryptophanato)-(2,2'-bipyridyl)-copper(ii) perchlorate)		5	[93]
Aqua-(L-tryptophanato)-(dipyrido[3,2-a:2',3'-c]phenazine)-copper(ii)nitrate methanol solvate		5	[94]
(di(2-pyridyl)amine)-(tryptophanato)-copper(ii) perchlorate dihydrate		4	[95]
catena-((PP)-(m2-L-tryptophanato)-(2,2'-bipyridyl)-copper(ii) perchlorate)		5	[96]
catena-((m2-4,4'-Bipyridyl)-bis(m2-L-tryptophanato)-diaqua-di-copper(ii)dinitrate)		5	[97]
Aqua-(6-deoxy-6-N-histamino-b-cyclodextrin-N,N')-(L-tryptophan-N,O)-copper(ii) tetradecahydrate	nitrate	5	[98]
Aqua-(dipyrido(3,2-a:2',3'-c)phenazine)-(L-tryptophanato)-copper(ii)perchlorate ethanol solvate monohydrate		5	[99]
catena-((MM)-(m2-L-tryptophanato)-(1,10-phenanthroline)-copper(ii)perchlorate trihydrate)		5	[100]

II.5. HISTIDINE

The crystal structure of bis-L-histidinecopper(II) dinitrate dehydrate has been determined [101]. The Cu(II) complexes of [Cu(tacn)(L-His)](PF₆)₂·H₂O (tacn = 1,4,7-triazacyclononane, L-His = L-histidine) are reported. Spectroscopic studies indicated the formation of the square pyramidal copper(II) complex [Cu(tacn)(L-His)]²⁺ which also revealed that the distorted square-pyramidal copper(II) coordination sphere is comprised of three nitrogen donors from the tacn macrocycle plus one carboxylate oxygen atom and the primary nitrogen atom from L-histidine [102]. The structure of dichloro(L-histidine)copper(II) has been reported. The structure consists of chains of molecules with the carboxy oxygen atom, the amino nitrogen atom and the two chlorine atoms forming an approximate square plane about the copper atom, with two bridging chlorine atoms from two adjacent molecules completing a distorted octahedron [103].

Compound	Coordination number	Ref.
bis(L-Histidine) copper(ii) nitrate dihydrate	6	[101]
(L-Histidine-N,O)-(1,4,7-triazacyclononane)-copper(ii)bis(hexafluorophosphate) monohydrate	5	[102]
Dichloro-(L-histidine)-copper(ii)	4	[103]
Dichloro-(3-(1H-imidazol-3-ium-5-yl)alaninato)-copper hemihydrate	4	[104]
(L-Histidine-N,O)-(1,10-phenanthroline)-copper(ii) diperchloratemonohydrate	4	[105]

II.6. LYSINE

The crystal and molecular structure of dichloro (d-lysinato (l-lysinato) copper (II) dehydrate has been investigated. The compound was prepared by reacting DL-lysine hydrochloride with basis copper carbonate. Single crystal, suitable for x-ray work, were obtained by slow evaporation of the resulting blue solution over a period of days. The coordination of the copper atom corresponds to a distorted octahedron with four short and two long bonds [106]. The crystal structure of bis(L-lysine)Cu(II) chloride dihydrate has been determined by X-ray analysis. The copper (II) atom has an essentially square planar coordination with the two lysine molecules chelated via the carboxy oxygen and the α -amino nitrogen [107].

Compound	Coordination number	Ref.
(d-Lysinato)-(l-lysinato)-copper(ii) dichloride dihydrate	4	[106]
Chloro-bis(L-lysinato-N,O)-copper(ii) chloride dihydrate	5	[107]
Chloro-bis(L-lysinato-N,O)-copper(ii) chloride dihydrate	5	[108]

II.7. LEUCINE

The crystal structures ternary complexes $[\text{Cu}(\text{L-Leu})(o\text{-phen})(\text{H}_2\text{O})]\text{NO}_3$ (1) and $[\text{Cu}(\text{DL-Leu})(o\text{-phen})(\text{H}_2\text{O})]\text{NO}_3$ (2) (Leu=leucinato and *o*-phen=1,10-phenanthroline), have been determined by X-ray diffraction. In each complex, the copper atom is coordinated in distorted squarepyramidal geometry by the bidentate Leu and *o*-phen ligands at the equatorial sites and water at an axial position. The isopropyl side chain of each Leu extends away from the aromatic ring system of *o*-phen, thus there is no intramolecular ligand-ligand interaction between them [109].

Compound	Coordination number	Ref.
bis(L-Leucinato) copper(ii)	4	[109]
Aqua-(L-leucinato-N,O)-(1,10-phenanthroline-N,N')-copper(ii) nitrate and Aqua-(DL-leucinato-N,O)-(1,10-phenanthroline-N,N')-copper(ii) nitrate	5	[110]
Aqua-(DL-leucinato)-(1,10-phenanthroline)-copper(ii) nitrate	5	[111]

II.8. ASPARTATE

Crystal structure of (L-aspartate)(imidazole)copper (II) dehydrate has been investigated. The copper atom shows a distorted square-pyramidal environment being linked to three different aspartate ions (one acting as bidentate ligand through the N(amino) and O(carboxylate) and the other as monodentate through the O of different carboxylate groups) and one imidazole molecule [112]. In the complex, $\{[\text{Cu}(\text{C}_4\text{H}_5\text{O}_4\text{N})(\text{C}_{10}\text{H}_9\text{N}_3)] \cdot \text{H}_2\text{O}\}_n$, the Cu atom has a distorted CuO_2N_3 square-pyramidal geometry formed by an *N,O*-bidentate aspartate (asp) anion and an *N,N*-bidentate 2,2'-bipyridylamine (bpa) molecule in the basal positions, and an *O*-monodentate asp ligand in the apical site. The complex forms a polymeric chain in which each metal centre is bridged to the next one by the asp anion [113].

Compound	Coordination number	Ref.
catena(L-Aspartate-imidazole-copper(ii) dihydrate	5	[112]
catena-((m2-L-aspartate-N,O,O)-(2,2'-bipyridylamine-N,N')-copper(ii)monohydrate)	5	[113]

II.9. PHENYLALANINE

For system Cu (L-Phe)(DA) [L-Phe; L-phenylalanine and DA = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen)] the difference absorption spectra in the region 320–400 nm exhibited a peak assignable to the charge transfer interaction between the aromatic rings of DA and L-Phe. The structures of [Cu (L-Phe)(phen)]Cl·3H₂O and [Cu(L-Phe)(bpy)]ClO₄·H₂O were determined by the X-ray diffraction method. The complexes have a similar distorted square-pyramidal structure around the central Cu (II) ion [114].

Compound	Coordination number	Ref.
Aqua-(1,10-phenanthroline-N,N')-(L-phenylalanine-N,O)-copper(ii) nitratemonohydrate	5	[114]
Chloro-(1,10-phenanthroline-N,N')-L-phenylalanine-copper(ii) trihydrate and Aqua-2,2'-bipyridine-L-phenylalanine-copper(ii) perchlorate monohydrate	5	[115]
bis((S,S)-N,N'-bis(2,5-Dimethoxybenzyl)cyclohexane-1,2-diamine)-(Dphenylalanine)-(trifluoromethanesulfonato)-copper(ii) N,N'-bis(2,5-dimethoxybenzyl)cyclohexane-1,2-diammoniumbis(trifluoromethanesulfonate) cyclohexane solvate	5	[116]
Aqua-(1,10-phenanthroline-5,6-dione)-(L-phenylalanine)-copper(ii)perchlorate monohydrate	5	[117]

II.10. VALINE

The X-ray crystal and molecular structures of *trans* bis(L-valinato)copper(II) and *cis* aquabis(L-valinato)copper(II) are presented. Heating of polycrystalline *cis* aquabis(L-valinato)copper(II) at 90 °C resulted in a dehydrated powder. Recrystallization from aqueous solution of the obtained product yielded anhydrous *trans* bis(L-valinato)copper(II) [130]. A **Novel copper (II) complex [Cu (L-val)(pmdt)]ClO₄ (L-val = L-valinate ion, and pmdt = N,N,N',N'',N''-pentamethyldiethylenetriamine) has been synthesized.** The complexes take on a *trans* (O_{amino acid}, N_{central of pmdt}) form, and their CuN₄O core geometries are approximately regular trigonal bipyramidal, which is novel for copper (II) complexes containing a discrete amino acid chelate ring [118].

Compound	Coordination number	Ref.
cis-aqua-bis(S)-valinato)-copper(ii)	5	[118]
(N,N,N',N'',N''-Pentamethyldiethylenetriamine)-(L-valinato)-copper(ii)perchlorate	5	[119]
aqua-(L-valinato)-(2,2'-bipyridyl)-copper(ii) nitrate dehydrate and (nitrato)-(L-valinato)-(1,10-phenanthroline)-copper(ii) dihydrate	5	[120]
Aqua-bis(L-valinato)-copper(ii)	5	[121]
Aqua-bis(L-valinato)-copper(ii)	5	[122]
Aqua-bis(L-valinato-N,O)-copper(ii)	5	[123]
catena-((m2-valinato)-(2,2-bipyridyl)-copper(ii) perchlorate monohydrate)	5	[124]
catena-(bis(m2-L-valinato)-(m2-4,4'-bipyridine)-diaqua-di-copper(ii)dinitrate)	5	[125]
(m2-4,4'-Bipyridine-N,N')-diaqua-bis((4,4'-bipyridine-N)-(L-valinato-N,O))-di-copper(ii) dinitrate dihydrate	5	[126]
Aqua-(1,10-phenanthroline)-(L-valinato)-copper(ii) chloridemonohydrate	5	[127]
Aqua-(1,10-phenanthroline)-(valinato)-copper(ii) nitrate dihydrate	5	[128]
catena-(trans-bis(m2-(S)-valinato)-copper(ii))	6	[129]

II.11. TYROSINE

The structure [Cu (L-Tyr)(phen)]ClO₄·2.5H₂O, isolated as crystals, was determined by the X-ray diffraction method. The ternary copper (II) complex [Cu(L-Tyr)(DA)] (L-Tyr=L-Tyrosin, DA = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) have been investigated. The difference absorption spectra in the region 320–400 nm exhibited a peak assignable to the charge transfer interaction between the aromatic rings of DA and L-Tyr. the complex has a similar distorted square-pyramidal structure around the central Cu(II) ion [143].

Compound	Coordination number	Ref.
Aqua-(1,10-phenanthroline-N,N')-L-tyrosine-copper(ii) perchloratesesquihydrate	5	[130]
Aqua-(1,4,8,9-tetra-azatriphenylene-N,N')-(L-tyrosine-N,O)-copper(ii)perchlorate monohydrate	5	[131]

II.12. GLUTAMINE

The molecular structure of a new copper (II) compound with the amino acid L-Glutamine, Cu [NH₂CO₂CH(CH₂)₂CONH₂]₂ has been reported. The Cu^{II} ion is in an elongated octahedral environment equatorially *trans*-coordinated by two glutamine molecules acting as bidentate ligands through the nitrogen atom and one oxygen atom of each amino acid group, and axially by two carboxylate oxygen atoms of two neighboring glutamine molecules [132]. For the first time, the structure of [Cu (II)(Gln)₂] has been determined in the solid state and in solution. X-ray crystal structure showed a 4-2 distorted octahedral geometry.

In the basal plane Cu–O and Cu–N distances ranged from 1.93 to 1.98 Å. Two additional oxygen atoms at 2.70 and 2.86 Å complete a severely distorted octahedron. EXAFS and EPR results have shown that the structure of [Cu (II)(Gln)₂] is preserved at physiological pH in aqueous solution [133].

Compound	Coordination number	Ref.
trans-bis(L-glutamine-N,O)-copper(ii)	4	[132]
trans-bis(L-glutamine-N,O)-copper(ii)	4	[133]
Aqua-(L-glutamine-N,O)-(1,10-phenanthroline-N,N')-copper(ii) chloridesesquihydrate	5	[134]

II.13. METHIONINE

The ternary Cu(II) complex with 2,2'-bipyridyl (bipy) and L-methionine (L-Met) has been synthesized. The crystal contains four crystallographically independent [Cu (L-Met) (bipy) (H₂O)]⁺ complexes (Cu1—Cu4), having a distorted square-pyramidal geometry with the same coordinated atoms around each copper center. The base plane is occupied by two nitrogen atoms of one bipy, the amino nitrogen atom and one carboxylate oxygen atom from each independent L-Met moiety, and one water oxygen at an axial position. Cu1 and Cu3 are essentially enantiomers of Cu2 and Cu4. The four molecules are packed with each other by intermolecular hydrogen-bonding and aromatic-ring stacking interactions [135].

Compound	Coordination number	Ref.
Aqua-(2,2'-bipyridyl)-(L-methionine)-copper(ii) perchlorate hydrate	5	[135]

II.14. ISOLEUCINE

A magnetic and structural characterization of single crystals of *trans*-bis (D,L-isoleucine) copper(II), was performed by EPR and X-ray diffraction techniques [136].

Compound	Coordination number	Ref.
trans-bis(D,L-Isoleucine-N,O)-copper(ii)	4	[136]
Aqua-(L-isoleucine-N,O)-(1,10-phenanthroline)-copper nitratemonohydrate	5	[137]

II.15. THREONINE

A novel ternary copper (II) complex, [Cu(phen)(L-Thr)(H₂O)](ClO₄) (phen = 1,10-phenanthroline, L-Thr = L-threonine), has been synthesized. The copper (II) center is situated in a distorted square-pyramidal geometry [138].

Compound	Coordination number	Ref.
Aqua-(1,10-phenanthroline)-(L-threonine)-copper(ii) perchlorate	5	[138]
bis-L-Threonine copper(ii) monohydrate	4	[139]

II.16. SERINE

Compound	Coordination number	Ref.
D,L,L,D-(2-Amino-3-hydroxypropanoato)-(2-aminobutanoato)-copper(ii)	4	[140]
(D)-2-Amino-3-hydroxypropanoato)-(L)-2-aminobutanoato)-copper(ii)	4	[141]
D-Serine-L-serine-copper(ii)	4	[142]

II.17. PROLINE

Compound	Coordination number	Ref.
Aqua(L-proline-L-alanine)-copper(ii) sesquihydrate	4	[143]

III. CONCLUSION

Amino acids are very important molecules made from amine (-NH₂) and carboxylic acid (-COOH) functional groups, with a side-chain specific to each amino acid. About 500 amino acids are known which can be classified in the functional groups' locations as alpha- (α -), beta- (β -), gamma- (γ -) or delta- (δ -) amino acids. Amino acids also perform critical biological roles including neurotransmitters, transport, and in synthesis. 20 of the 22 proteinogenic amino acids are called standard amino acids-those found in human beings. This review gives an overview on structures and Coordination chemistry of copper complexes with 17 of the 20 standard amino acids. A comprehensive review, >120 references, on copper complexes of the amino acids is presented.

ACKNOWLEDGEMENTS

Support of this work by the Payame Noor University is gratefully acknowledged.

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