Chiral Selectivity in the Basic or Acid α-amino Acids Homomeric Cu(II) Complexes Range

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Plan-tetragonal coordination in copper (II) complexes of basic and acid α-amino acids generates diastereomers having structures and solubility influenced by the nature and charge of the counter-ions, which can complex intra or inter-molecular with charged functional groups belonging to lateral catena of the ligands. Stereochemical selectivity correlates with the charge and solubility correlates with the capacity to achieve hydrogen bonds. The complexes structures depend on the chirality of the ligands involved in coordination. On this basis, is possible the chiral separation by selective crystallization of the hetero-chiral diastereomers from the homo-chiral one.

Keywords: amino acid copper complex, chiral diastereomers, anion complexation, chiral separation

All natural α-amino acids form stable complexes type $[(AA)_2Cu]$ (where AA means deprotonated amino acid) with Cu^{2+} having a plan-tetragonal coordination geometry. Both AA ligand molecules close penta-atomic rings using α-amino N and carboxylic O[1].

Several authors[2 - 4] proved that the ε-amino in Lys (lysine), δ-guanidine in Arg (arginine) and γ-carboxylate in Glu (glutamic acid) do not participate to coordination. There are proofs that δ-amino in Orn (ornithine) and β-carboxylate in Asp (aspartic acid) coordinate in apical position[5].

The tetragonal coordination geometry, involving chiral ligands, generates homo and heterochiral diastereomers having the structure determined by the *cis* or *trans* position of donor atoms, N and O, against complex generator [4]. The lateral catena are situated, function of the α-C chirality, on the same side of the coordination plan (*syn*), for L,L-*trans* and L,D-*cis* complexes, but on one and another side of the coordination plan (*anti*) for L,L-*cis* and L,D-*trans* (fig. 1).

Calorimetric determinations and molecular mechanic calculations[6-8] proved that the *trans* structures are thermodynamically favored.

The reciprocal position of lateral catena, achieved after complex formation, can determine specific interactions between them [2, 9]. The interactions can be steric (fitting or repulsion), electrostatic (attraction or repulsion), hydrogen bonds and another [10]. They can manifest oneself intra or inter-molecular, their complexity being amplified by the interactions with the solvent and another particles present and it depends on the concrete conditions of reaction mixture (concentration, pH, temperature, ionic strength). The situation has some analogy with polypeptides [11].

Basic α-amino acids (Lys and Arg), in close proximity of neutral *p*H (for instance, physiologic *p*H, 7.45) present the ω-amino, respectively, guanidine protonated, that is, having a positive charge. In same conditions, the acid AA Glu and Asp present ω-carboxyl deprotonated, under

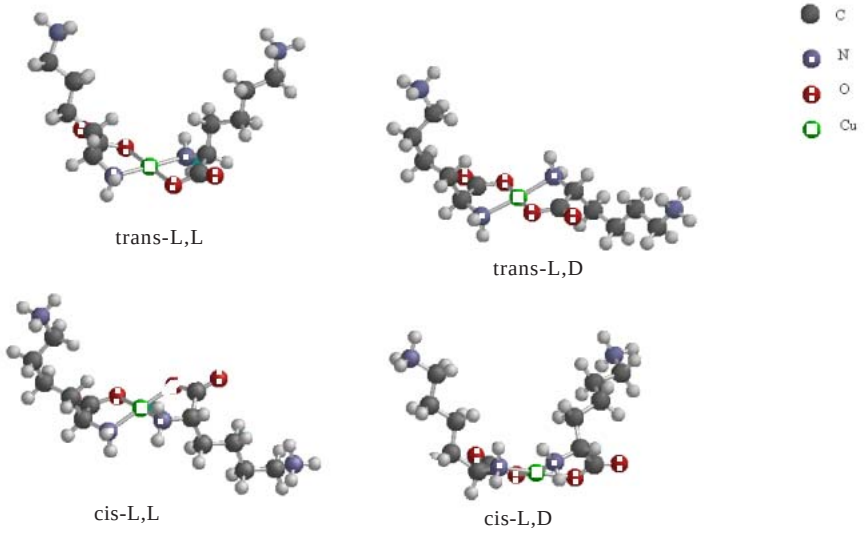

Fig. 1. Possible structure of the stereomeric complexes $[(Lys)_2Cu]^{2+}$ (*trans-L,L; trans-D,L; cis-D,L; cis-L,L*)

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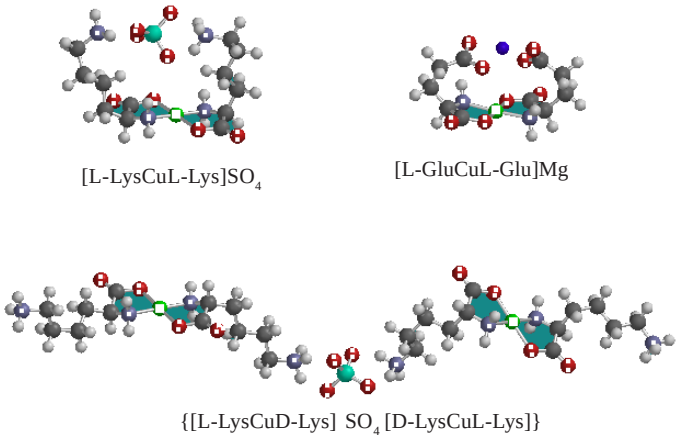

Fig. 2. Possible structures in the interaction of $[(AA)_2Cu]^{2+}$ and $[(AA)_2Cu]^{2-}$ complexes with the counter-ions in solution

carboxylate form [12]. Repulsion could manifest between the two charges belonging to both catenas, brought in proximity by complexation, in ideal conditions (individual molecules in vacuum) and influenced by the structure *cis-trans, syn-anti*. In real conditions, the charges are, of course, compensated by counter-ions, and the molecules are solvatated.

In the case of homomeric complex with basic or acid AA, electrostatic repulsion is changed in attraction, by the insertion of the counter-ions having opposite charge. For example, in Lys or Arg case, the both groups positively charged, ε-ammonium or δ-guanidinium, in favorable steric conditions, can be *coordinated* by an *anion complex generator* (better by a divalent anion) which can stabilize the intramolecular relation, forming a *complex* of the anion with the lateral catena of the AA ligands, already involved in the complex with Cu^{2+} "at another end" [13-15] (fig. 2). The situation is, accordingly, the same in acid AA case, when carboxylate groups from laterally catena can be secondarily coordinated by another cation [16] (fig. 2).

The structures *syn*, having the laterally catena at the same side of coordination plan, (*trans*-L,L and *cis*-D,L) present a much bigger probability for intra-molecular compensation because the charges are situated in a favorable position. The structures *anti* encourage inter-molecular compensation.

The well fitted counter-ion charge, equal in absolute value with the sum of the charges belonging to the lateral catena, stabilizes the discrimination between intra-molecular and inter-molecular compensation.

Chiral selectivity can be considered like an example of molecular recognition in supramolecular structures. Jean-Marie Lehn, in his book "Supramolecular chemistry. Concepts and perspectives" [16] proves that a high selectivity suppose a big difference of affinity between supramolecular constructions which can be obtained in concrete conditions. To attain this affinity difference there are a lot of factors involved. Analyzing the degree of these factors involvement in the case of homomer Cu^{2+} complexes with arginine, lysine and glutamic acid, we found out the following:

- steric complementarities (form and dimensions) between the substrate (the homomer-homochiral or homomer-heterochiral diastereomer) and the receptor (counter-ions) - The structures *syn* (homochiral), having the lateral catena, carrying charges of the same sign and on the same side of the chelatization plane, present a bigger conformational probability of intra-molecular compensation with a counter-ion of relative small dimension. The structures *anti*, on the contrary, favour the inter-molecular compensation. This aspect is the base of chiral selectivity in the analyzed case;

- interactional complementarities — Are achieved, in our case, by the electrostatic attraction between the charges of opposed sign. The charge 2 of the counter-ion is the most favorable. In addition to that, between counter-anions (specially oxygenated ones) and ammonium or guanidinium groups belonging to lysine and arginine ligands can be established a lot of hydrogen bonds which strengthen supplementary the structure;

- contact surface as great as possible — Conformational mobility of the ligands catena allows the achievement of low energy structures;

- multiple interaction positions — The anions containing more oxygen atoms can make multiple hydrogen bonds;

- the sum of all bonding energies (all types) to be as high as possible — Even if stability do not means direct selectivity, more irreversibility provides better selectivity. So, we can expect maximum selectivity in the case of arginine complexes with tetra-oxygenated anions.

The application of selectivity criteria in our case indicates real possibilities of chiral selectivity.

In the specialty literature, there are many studies regarding the chiral selectivity in the family of natural AA with Cu(II). The correlation of stability constants of ternary complexes with thermodynamic data of forming reaction [17] in the case of Cu(II) complexes with hystidine and other AA and with the selectivity like difference of stability was discussed. The driving force of chiral selectivity is considered to be electrostatic attraction between opposed charges from the lateral catena of heteromeric diastereomers.

Many studies were accomplished in connection with chiral HPLC application by ligands exchange, the chiral selectivity being attributed also to the relation between lateral catena of the ligands (electrostatic, steric, π–π) [18]. Other studies about chiral selectivity in the case of ternary complexes of copper with AA basic and acid was published by a Japanese team[19 - 23] which explained the selectivity by the electrostatic attraction between lateral catena having opposed charges in an intra-molecular relation, by the exaltation of circular dicroism magnitude because of structure rigidization. Chiral separation of racemic mixtures of acid AA using basic AA and vice versa (heteromeric complexes) was studied.

Experimental part

The following compounds were synthesized:

- Lysine complex type $[Cu(AA)_2]^{2+}$ having like counter-anions chloride, carbonate, sulphate and phosphate.

- Arginine complex, same type, with chloride, acetate, nitrate, perchlorate, carbonate, oxalate, sulphyte, sulphate, posphate.

- Glutamic acid complex type $[Cu(L\text{-}Glu)_2]^{2-}$ having counter-cations sodium, calcium, barium, magnesium, tetraethylethylendiammonium .

For these purposes there were used chemicals *p.a.* and the general, following procedure was put into practice:

2 mmolls of L-AA or 1 mmoll of L-AA and 1 mmoll of D-AA is dissolved (or suspended) in 2 mL of water. The pH is adjusted at 7 – 7.5 with $Ba(OH)_2$, LiOH, NaOH without carbonate, Na_2CO_3 anhydrous, CaO, tetraethylethylen-diamine (TEEDA), and HCl, HNO_3, H_2SO_4, $HClO_4$, solution 6% SO_2 in water, NaH_2PO_4, acetic acid, oxalic acid, function of the wanted counter-ion. 1 mmoll $CuCl_2$ anhydrous is added and the pH is readjusted at 7 – 7.5 with NaOH 2.5N without carbonate, Na_2CO_3 anhydrous, and with NaOH

2,5N, solid $Ba(OH)_2$, solid CaO, and TEEDA in the case of acid amino acid. Stir 10 min at 50°C, then leave to arrive at room temperature, without stirring, watching the precipitate appearance at 0.5, 6 and 24 h. Crystals of soluble diastereomeres were obtained by slow solvent evaporation.

UV-Vis spectra, in watery solution, FTIR spectra in powder, for same representative complexes and X-ray structure determinations for a homochiral diastereomers $[Cu(L\text{-}Arg)_2H_2O]CO_3 \cdot H_2O$ and a heterochiral one have been carried out $[Cu(L\text{-}Lys)(D\text{-}Lys)]Cl_2 \cdot H_2O$.

Results and discusions

The crystallization (precipitation) tendency of formed complexes, immediately after reaction (0.5 h) and after a longer time (6 and 24 h) is summarized in table 1.

We succeeded to obtain monocrystals suitable for X-ray structure determination of $[Cu(L\text{-}Arg)_2(H_2O)]CO_3 \cdot H_2O$, figure 3 and table 2, and $[Cu(L\text{-}Lys)(D\text{-}Lys)]Cl_2 \cdot H_2O$, figure 4 and table 3.

The examination of experimental data enables us to observe same interesting tendencies regarding the solubility (precipitation tendency) and diastereomeric selectivity (the solubility difference between homo and heterochiral diastereomers):

- crystallization tendency increases in parallels with the capacity of anions to make hydrogen bonds. The solubility of arginine complexes with monovalent anions decreases abruptly from Cl^- and acetate, which do not precipitate even after very long storage time, to NO_3^- which has tree oxygen atoms able to participate in hydrogen bonds and induces precipitation after 2-6 h, and, arriving at ClO_4^- which, with four oxygen atoms possibly involved in hydrogen bonds, causes immediate precipitation;
- the selectivity, that is the solubility difference between hetero and homochiral complexes, depends upon the counter-anion charge. If for monovalent anions this difference is hardly to notice, hetero-chiral complex having, nevertheless, a slight higher precipitation tendency, the

Table 1
PRECIPITATION TENDENCY OF COMPLEXES, FUNCTION OF CONTER-ION TYPE

No.	Counter-ion	Complex type	Precipitate after 0,5 h	Precipitate after 6 h	Precipitate after 24 h	
1	Cl^-	L-K Cu L-K	no	no	no	
2	Cl^-	L-K Cu D-K	no	no	yes	
3	CO_3^{2-}	L-K Cu L-K	no	yes	yes	
4	CO_3^{2-}	L-K Cu D-K	yes	yes	yes	
5	SO_4^{2-}	L-K Cu L-K	no	no	no	
6	SO_4^{2-}	L-K Cu D-K	no	yes	yes	
7	PO_4^{3-}	L-K Cu L-K	no	no	no	
8	PO_4^{3-}	L-K Cu D-K	no	no	no	
9	Cl^-	L-R Cu L-R	no	no	no	
10	Cl^-	L-R Cu D-R	no	no	no	
11	Ac	L-R Cu L-R	no	no	no	
12	Ac	L-R Cu D-R	no	no	no	
13	NO_3^-	L-R Cu L-R	no	no	yes	
14	NO_3^-	L-R Cu D-R	no	yes	yes	
15	ClO_4^-	L-R Cu L-R	yes	yes	yes	
16	ClO_4^-	L-R Cu D-R	yes	yes	yes	
17	CO_3^{2-}	L-R CuL-R	no	no	no	
18	CO_3^{2-}	L-R Cu D-R	no	yes	yes	
19	Ox	L-R Cu L-R	no	no	yes	
20	Ox	L-R Cu D-R	no	yes	yes	
21	SO_3^{2-}	L-R Cu L-R	no	no	no	
22	SO_3^{2-}	L-R Cu D-R	no	yes	yes	
23	SO_4^{2-}	L-R Cu L-R	no	no	no	
24	SO_4^{2-}	L-R Cu D-R	no	yes	yes	
25	PO_4^{2-}	L-R Cu L-R	no	no	no	

26	PO_4^{2-}	L-R Cu D-R	no	no	no	
27	Na^+	L-E Cu L-E	no	no	no	
28	Na^+	L-E Cu D-E	no	no	no	
29	Ca^{2+}	L-E Cu L-E	no	no	no	
30	Ca^{2+}	L-E Cu D-E	no	no	no	
31	Ba^{2+}	L-E Cu L-E	no	no	no	
32	Ba^{2+}	L-E Cu D-E	no	no	no	
33	$TEEDA^{2+}$	L-E Cu L-E TEEDA	no	no	no	
34	$TEEDA^{2+}$	L-E Cu D-E TEEDA	no	no	no	

Note: K = Lys = Lysine, R = Arg = Arginine, E = Glu = Glutamic acid, Ac = CH_3COO^-, Ox = $(COO)_2^{2-}$ = Oxalate, TEEDA = tetraethylethylendiamine.

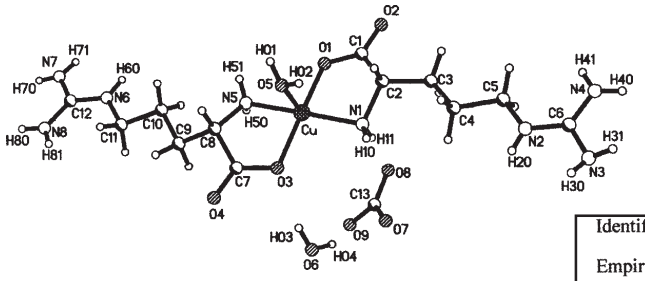

Fig. 3. X-ray structure of $[Cu(L\text{-}Arg)_2(H_2O)]CO_3 \cdot H_2O$

Table 2
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $[Cu(L\text{-}Arg)_2(H_2O)]CO_3 \cdot H_2O$

Identification code	ineda	
Empirical formula	$C_{13}H_{32}CuN_8O_9$	
Formula weight	508.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.3467(2) Å	α= 90°
	b = 12.0931(2) Å	β= 94.887(2)°
	c = 10.1911(2) Å	γ = 90°
Volume	1024.92(4) Å^3	
Z	2	
Density (calculated)	1.646 Mg/m^3	
Absorption coefficient	1.132 mm^{-1}	
F(000)	534	
Crystal size	0.27 x 0.12 x 0.07 mm^3	
Theta range for data collection	2.62 to 31.00°	
Index ranges	-12<=h<=12, -17<=k<=17, -14<=l<=14	
Reflections collected	27674	
Independent reflections	6467 [R(int) = 0.0371]	
Completeness to theta = 31.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.91464	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6467 / 98 / 352	
Goodness-of-fit on F^2	1.012	
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0535	
R indices (all data)	R1 = 0.0268, wR2 = 0.0541	
Absolute structure parameter	0.002(6)	
Largest diff. peak and hole (gap ?)	0.327 and -0.345 e.Å^{-3}	

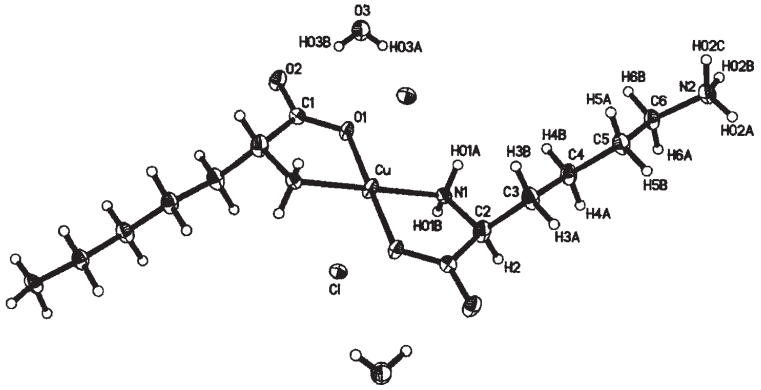

Fig. 4. X-ray structure of [Cu(L-Lys)(D-Lys)]$Cl_2 \cdot H_2O$ complex

Identification code	bac01	
Empirical formula	$C_{12}H_{32}Cl_2CuN_4O_6$	
Formula weight	462.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_1/n$	
Unit cell dimensions	a = 5.1165(2) Å	α= 90°
	b = 17.2036(9) Å	β= 96.691(4)°
	c = 11.3504(6) Å	γ = 90°
Volume	992.28(8) Å^3	
Z	2	
Density (calculated)	1.549 Mg/m^3	
Absorption coefficient	1.404 mm^{-1}	
F(000)	486	
Crystal size	0.14 x 0.04 x 0.04 mm^3	
Theta range for data collection	2.16 to 26.36°	
Index ranges	-6<=h<=6, -21<=k<=21, -14<=l<=14	
Reflections collected	23796	
Independent reflections	2031 [R(int) = 0.0608]	
Completeness to theta = 26.36°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92566	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2031 / 0 / 143	
Goodness-of-fit on F^2	0.939	
Final R indices [I>2sigma(I)]	R1 = 0.0290, wR2 = 0.0642	
R indices (all data)	R1 = 0.0412, wR2 = 0.0661	
Largest diff. peak and hole	0.697 and -0.358 e.Å^{-3}	

Table 3
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR [Cu(L-Lys)(D-Lys)]$Cl_2 \cdot H_2O$

discrimination induced by the divalent anions is clear. The hetero-chiral complex of Arg with sulphate like anion precipitates totally and the homochiral one not at all;

- even if between functional groups ω-amino and guanidine there is a great difference regarding the structure, the basicity and capacity to make hydrogen bonds, the behaviour of both AA is similar;

- phosphate anion, although it has 4 oxygen atoms, does not induce precipitation and, even if it has negative charge 3, it does not ensure selectivity;

- for glutamic acid complexes, in our experimentally conditions, it was not observed any difference connected with the nature and charge of the cation. All of them have a great solubility, and when the solvent evaporates, they form a glassy solid structure.

The majority of synthesized compounds are known and characterized in literature. For a lot of them the X-ray structures are determined (especially for homochiral ones) [24].

The UV-Vis spectra in water solution, made for representative compounds homo and hetero-chiral do not give arguments about the *cis* or *trans* structure in the first coordination sphere. It may be possible that, knowing the great speed of the ligand change reaction for this complexes, to be a dynamic equilibrium between the both structures[25].

The FTIR spectra, carried out on powder, in the range 600-4000 cm^{-1} did not include the wavelength domain for the Cu-N and Cu-O stretch vibrations, in order to be able to conclude about the *cis* or *trans* structure.

The X-ray structure for $[Cu(L\text{-}Arg)_2H_2O]CO_3$, found also in literature [24], and $[Cu(L\text{-}Lys)(D\text{-}Lys)]Cl_2 \cdot H_2O$, not found in literature, by difference, are conclusive regarding the *cis* or *trans* and *syn* or *anti* structure. Even if these structures represent only the last step in crystallization process, they can suggest the mechanism of chiral selectivity. It can ascertain that the coordination is *trans* in both cases and the position of laterally catena is *syn* for the homochiral complex and *anti* for the heterochiral one. So, the tendency of homochiral diastereomers to compensate the both positive charges from lateral catena intramolecular (being situated on the same side of chelatization plane), and intermolecular for the heterochiral diastereomers (having the catena charges at higher distance, on opposite sides of chelatization plane) can be explained.

When the counter-anion is monovalent, an exclusive intramolecular compensation is not possible and does not achieve the different solubility between enantiomers.

When it is bivalent, the compensation for the homochiral diastereomers is mostly intramolecular, the realized structure having a very small aggregation tendency, that is, a bigger solubility, in contrast with that heterochiral case which compensates the charges intermolecular, ensuring aggregation and crystallization. Because between ammonium and guanidinium groups from lateral catena, and oxygen atoms from counter-anions multiple hydrogen bonds are established, all the structures are supplementary stabilized.

The trivalent anions exceed the need of intramolecular compensation, achieving, probably, through the third negative charge, intermolecular association of another complex molecule into small symmetry structure having a low crystallization tendency. Without precipitation tendency, we do not expect selectivity.

Conclusions

In this work we proposed to study the influence of nature and charge of the ions (counter-ions) present in reaction mixing, on the possibility of chiral separation by selective crystallization.

The results suggest the tendency of homochiral diastereomers (L,L and D,D) to compensate positive charges from the lateral catena by intramolecular complexation of anions, in contrast with heterochiral diastereomers (L,D) which achieve electrostatic neutrality preferably by intermolecular coordination.

Solubility decreases with the increasing number of oxygen atoms in the anion composition (increase of the probability of hydrogen bonds), and the selectivity increases abruptly with changing the charge from -1 to-2. Maximum selectivity is obtained with tetra-oxygenated di-anions.

Chiral separation or purification by selective crystallization of basic AA can be done using Cu^{2+} diastereomeric complex having SO_4^{2-} or CO_3^{2-} contra-anions.

Chiral separation by selective crystallization using homomeric complexes, after our knowledge, was not studied.

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