



**TRANSITION METAL COMPLEXES OF AMINO ACID AND
PEPTIDE DERIVATIVES CONTAINING CARBOXYLATE AND
IMIDAZOLE SIDE CHAINS**

Propositions of PhD thesis

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I. INTRODUCTION AND THE AIM OF THE WORK

It is well known that some metal ions are essential for living organisms. They play important roles in the synthesis and transport of organic molecules and in catalyzing acid-base and redox processes of biological systems.

In metalloenzymes metal ions are usually bound by the side chain donor functions of the peptides. The N(1)/N(3) donor atoms of histidyl and carboxylate groups of the aspartyl and glutamyl residues are especially preferred binding sites of metalloenzymes.

The role of the side chain carboxylate groups on the metal ion coordination of peptides and peptide derivatives has already been widely studied. The data indicate that the effect of the carboxylate groups on the complex formation processes depends on the number and location of these amino acids in the peptide chain.

The effect of the location of these amino acids in the peptide chain on the complex formation processes has already been widely studied. However the presence of carboxylate groups in the side chain modifies the charge of the ligands and the complexes. We have investigated the copper(II) and nickel(II) complexes of di-, tri- and tetra-peptides containing one, two or more aspartic and/or glutamic acids. We have studied the influence of β - and γ -carboxylate group as well as *the effect of increased negative charge of complexes*.

The carboxylate group in the side chain of aspartic and glutamic acid also can be involved in amide binding. The peptide-amide bonds formed by the β - and γ -carboxylic groups of aspartic and glutamic acids are separated from the peptide backbone providing new coordination environments for metal ions. Lysine has similar property; the ϵ -amino group can also form a peptide bond with the carboxylic group of another amino acid, like in the case of Asp- ϵ -Lys, or both amino groups of lysine can be involved in amide bound like in the case of Gly-Lys(Gly). We have investigated the copper(II), nickel(II) and zinc(II) complexes of these two peptides. We have studied *the effect of the peptide bond formed by ϵ -amino group*.

The studies of ligands containing bis(imidazol-2-yl) group started about 15 years ago. They studied the coordination chemistry of the simplest ligands, then the N-protected tripeptide derivatives and the effect of the groups in chelatable position on the amino acid and peptide derivatives. However, the effect of carboxylate group in the side chain were not known. We have investigated the coordination chemistry of ligands containing bis(imidazol-2-yl) group on the C-terminus and a carboxylic group in the side chain comparing with the simplest dipeptides and the simplest amino acid derivatives of bis(imidazol-2-yl)methane. Moreover these ligands can mimic the active site of metalloenzymes.

Therefore studies were continued into two directions. First of all we have investigated the coordination chemistry of bis(imidazol-2-yl) derivatives containing aspartic and glutamic acid. We have studied *the effect of the side chain carboxylate group on the complexation of amino acid bis(imidazol-2-yl)methyl derivatives via the ligands α -aspartyl-bis(imidazol-2-yl)methylamine (α -Asp-BIMA), α -glutamyl-bis(imidazol-2-yl)methylamine (α -Glu-BIMA) and γ -glutamyl-bis(imidazol-2-yl)methylamine (γ -Glu-BIMA)*. On the other hand we tried to mimic Cu,Zn-SOD with other peptides.

In the active site of Cu,Zn-SOD both binding sites mentioned earlier are found; the ions are coordinated by the carboxylate group of aspartic acid and the imidazole nitrogens of histidine. The protein part of the enzyme which is included in the metal ion binding can be mimicked with oligopeptides. For this reason *we synthesized peptides containing histidine and aspartic acid (Ac-His-Ala-His-Val-His-NH₂, Ac-His-Val-His-Ala-His-NH₂, Ac-His-Pro-His-Ala-His-NH₂, Ac-His-Ala-His-Pro-His-NH₂, Ac-His-Val-Gly-Asp-His-NH₂ and Ac-His-His-Val-Gly-Asp-NH₂). We characterized the coordination chemistry of these peptides with copper(II) ions.*

II. EXPERIMENTAL METHODS

Protonation constants of the ligands and the stability constants of the metal complexes were determined by potentiometric titration ($T = 278 \text{ K}$, $I = 0.2 \text{ mol-dm}^{-3} \text{ KCl}$). The evaluations of titration curves were performed by PSEQUAD and SUPERQUAD computational programs. In order to determine the protonation microconstants ¹H NMR technique was used. For characterization of the binding modes in the complexes UV-Visible spectrophotometric, circular dichroism (CD) and electron paramagnetic resonance (EPR) spectroscopic methods were applied.

Peptides containing aspartic and glutamic acid and oligopeptides containing ϵ -amide bond (*Scheme 1*) were purchased from Bachem. The amino acid derivatives of bis(imidazol-2-yl) methyl residue (*Scheme 2*) were prepared in the Research group of Peptide Chemistry of ELTE-MTA. The ligands related to the active site of Cu,Zn-superoxide dismutase were synthesized in the solid state at the University of Ioannina, Greece.

III. RESULTS

The studied ligands can be divided into four groups:

1. Oligopeptides containing aspartyl and glutamyl residues

We studied copper(II) complexes of thirteen di- tri- and tetra-peptides built up from Asp and/or Glu residues (Asp-Ala, Ala-Asp, Asp-Val, Val-Asp, Glu-Val, Val-Glu, Asp-Glu, Glu-Asp, Asp₂, Glu₂, Asp₃, Glu₃ and Asp₄). In the case of the five last peptides experiments were carried out also with nickel(II) ions.

1.1. These ligands contain two to five carboxylate functions, which results in the enhanced metal binding ability of the peptides, it is especially true for the oligopeptides of aspartic acid. In the case of peptides containing aspartyl residue in the N-terminal position the stability enhancement is reflected by the equilibrium data of the species ML containing the (NH₂, β -COO⁻)-coordination mode in a 6-membered chelate.

1.2. In the case of Asp₂ and Asp₃ the (NH₂,N⁻, β -COO⁻) and (NH₂,N⁻,N⁻, β -COO⁻) coordination modes will be favoured, which contain (5,6) and (5,5,6) joined chelate ring

systems, respectively. The outstanding stability of the latter binding mode and the high negative charge of the corresponding species suppress the metal ion coordination of the third amide function of Asp₄. These findings are true for both copper(II) and nickel(II) ions.

1.3. γ -carboxylate group of glutamic acid would form a seven-membered chelate ring, which is not favourable. Therefore its weak interaction with the metal ions results only in slight increase of the stability of the complexes, but in the case of Glu₃ the increased negative charge of the CuL complex results in the decrease of its stability.

1.4. It is also important to note that the presence of side chain carboxylate functions results in the formation of carboxylato-bridged polynuclear complexes in medium pH range. The extent of oligomerisation can be significantly enhanced by the increase of concentration and by the decrease of temperature.

2. Oligopeptides containing ε -amide bond

We studied the copper(II), nickel(II) and zinc(II) complexes of two oligopeptides containing the amide bond on the ε -amino group of lysine, namely α -Asp- ε -Lys and Gly-Lys(Gly). The peptide amide bonds formed by the ε -amino groups of lysine are separated from the peptide backbone creating new coordination environments for metal ions.

2.1. The coordination chemistry of Asp- ε -Lys is the best characterized by the presence of amino acid binding sites similarly to those of α - and β -alanine. In addition, it can behave as a substituted glycineamide with very high affinity for dimerisation. The stoichiometries of the dinuclear complexes can be given as $[M_2L_2]$ ($2[(NH_2,COO^-)(NH_2,COO^-)]$ coordination) (*Scheme 3.a*) and $[M_2L_2H_2]^{2-}$ ($2[(NH_2,N^-)(NH_2,COO^-)]$ coordination) (*Scheme 3.b*). In the case of copper(II) the formation of both dinuclear species has been detected in agreement with the high affinity of copper(II) for binding to amide nitrogens of peptides. However, in the nickel(II)- and zinc(II)-Asp- ε -Lys systems only the species $[M_2L_2]$ was detected containing the amino acid like binding mode and suppressing deprotonation of both amide groups and coordinated water molecules.

2.2. In Gly-Lys(Gly) both amino groups of lysyl are bounded to glycines. Thus this ligand is built up from 3 amino acids, but its coordination chemistry is completely different from those of common tripeptides. It can coordinate to the metal ions via the amino and carbonyl groups at both termini or after the deprotonation of the amide functions it can be considered either as a substituted dipeptide or a substituted glycineamide. The stoichiometry of the major species is $[CuLH_{-1}]$ in the copper(II)-Gly-Lys(Gly) system and the EPR spectroscopy unambiguously prove the existence of two isomeric forms (*Scheme 4.a and 4.b*) of the complex. The extra stability of these isomers arises from the formation of chelate rings coupled via a macrochelate ($(NH_2,CO)(NH_2,N^-)$ and $(NH_2,N^-,COO^-)(NH_2,CO)$ coordination) and suppresses hydrolytic reactions. Deprotonation and coordination of the amide nitrogens were, however, detected only in the copper(II) and nickel(II) complexes of Gly-Lys(Gly).

2.3. The nickel(II)- and zinc(II)-Gly-Lys(Gly) systems have been characterized by the formation of stable $[ML]^+$ complexes (*Scheme 4.c*) and the increased stability of these species was explained by the bis(NH_2,CO) coordination coupled via a macrochelate.

3. Amino acid derivatives of bis(imidazol-2-yl)methyl residue

We have investigated the effect of side chain carboxylate group on the complexation of amino acid-bis(imidazol-2-yl) derivatives via the ligands α -Asp-BIMA, α -Glu-BIMA, γ -Glu-BIMA and for comparison β -Ala-BIMA.

3.1. With *copper(II)* ions the complex formation processes start in very acidic solution ($\text{pH} \leq 2$), and the bis(imidazol-2-yl)methyl residue is the exclusive binding site in this pH region.

The side chain donor groups of amino acids form six- or five membered chelate rings with terminal amino group and this results in the formation of isomers of dinuclear complexes with ligand bridging. It was observed in the case of α -Asp-BIMA (*Scheme 5.a and 5.b*) and γ -Glu-BIMA.

For all amino acid derivatives, in which the terminal amino and the deprotonated amide nitrogen can form five- or six membered chelates, the deprotonation of amide nitrogen takes place at slightly acidic pH (above pH 6), and the coordination of ($\text{NH}_2, \text{N}^-, \text{Im}(\text{N})$) donor set is able to break the bis(imidazol-2-yl)methyl coordination mode. It results in the formation of dinuclear $\text{Cu}_2\text{L}_2\text{H}_{-2}$ species, in which one of the imidazole rings of bis(imidazol-2-yl)methyl moiety serves a bridge (*Scheme 5.c*). This process, however, does not occur in the case of γ -Glu-BIMA, in which the amino and amide nitrogen could form only seven membered chelate ring.

3.2. A new base consuming process can be observed in alkaline solution. This process can be explained by mixed hydroxo complex formation in the case of amino acid derivatives with non-coordinating side chain (β -Ala-BIMA), and the deprotonation of pyrrole type nitrogen of ligands containing side chain donor group (α -Asp-BIMA and α -Glu-BIMA). As a consequence, the presence of side chain donor group can prevent the hydrolysis of copper(II) complex, probably because of its weak interaction with copper(II) ion. The deprotonation of the pyrrole type nitrogen creates a new metal ion binding site, which leads to the existence of a trinuclear $\text{Cu}_3\text{L}_2\text{H}_{-4}$ complex with negatively charged imidazolate bridge in the Cu(II)- α -Asp-BIMA (*Scheme 5.d*) and Cu(II)- α -Glu-BIMA systems at 3:2 molar ratio. The formation of trinuclear species also can be supposed for Cu(II)- β -Ala-BIMA at excess of metal ion.

3.3. The stoichiometries of the *nickel(II) and zinc(II) complexes* are very similar to those of copper(II) complexes, but these species have much lower thermodynamic stabilities, which shifts the complex formation reactions to higher pH values. As a consequence, the concentration of protonated complexes is much lower, especially in the case of zinc(II), and the stability of the complexes decreases in the order $\text{Cu(II)} > \text{Ni(II)} > \text{Zn(II)}$ according to the Irving-Williams series.

3.4. For nickel(II) and zinc(II) ions the bis(imidazolyl) residues were detected as the major metal binding sites in acidic solutions, similarly to copper(II), but the low ratio of the stepwise stability constants shows some differences in the binding modes of copper(II) and nickel(II) or zinc(II) complexes. Namely, protonated bis(ligand) complexes of copper(II) were described by the equatorial coordination of 4N donor atoms, while the regular octahedral geometry of nickel(II) and zinc(II) complexes provides a more flexible coordination environment. Therefore the amount of bis(ligand) complexes is higher. On the other hand, the relatively high stability of bis(ligand) complexes slightly suppresses amide deprotonation in

the corresponding nickel(II) and zinc(II) complexes as compared to that of copper(II) species. The concentration of dimer complexes with these ions are also lower, and in the Ni(II)- α -Asp-BIMA system following the deprotonation of amide nitrogen a monomer \rightleftharpoons dimer equilibrium exists.

3.5. In the case of α -Glu-BIMA and γ -Glu-BIMA besides deprotonation macroconstants we have also calculated deprotonation microconstants of these ligands. In α -Glu-BIMA the deprotonation sequence is $\text{Im}_1 \rightarrow -\text{COOH} \rightarrow \text{Im}_2 \rightarrow -\text{NH}_3^+$ and the deprotonation processes significantly overlap. In γ -Glu-BIMA this sequence is $\text{COOH} \rightarrow \text{Im}_1 \rightarrow \text{Im}_2 \rightarrow -\text{NH}_3^+$ and the deprotonation processes are separate.

4. Pentapeptides related to the active site of Cu,Zn-superoxide dismutase

We have characterized the copper(II) complexes of pentapeptides (Ac-His-Ala-His-Val-His-NH₂, Ac-His-Val-His-Ala-His-NH₂, Ac-His-Pro-His-Ala-His-NH₂, Ac-His-Ala-His-Pro-His-NH₂, Ac-His-Val-Gly-Asp-His-NH₂ and Ac-His-His-Val-Gly-Asp-NH₂) which were synthesized for modeling the metal binding sites of the Cu,Zn-SOD enzyme,.

4.1. These ligands have very efficient binding sites. In acidic solution CuL macrochelates form, in which three histidine nitrogens or two histidine nitrogens and one aspartate oxygen are coordinated (*Scheme 6.a*). These binding modes result higher stability and shift the formation of this complex to higher pH range.

4.2. Above pH 7 the deprotonation and coordination of amide nitrogens take place resulting in isomer CuLH₂ and CuLH₃ complexes in the case of Ac-His-Ala-His-Val-His-NH₂, Ac-His-Val-His-Ala-His-NH₂ and Ac-His-His-Val-Gly-Asp-NH₂. However, only one complex structure is possible in the case of Ac-His-Val-Gly-Asp-His-NH₂ and with the peptides containing proline.

4.3. Ac-His-Ala-His-Val-His-NH₂ and Ac-His-Val-His-Ala-His-NH₂ are able to bind two equivalent copper(II) ion and Cu₂LH₂, Cu₂LH₄, Cu₂LH₅ and Cu₂LH₆ complexes form (*Scheme 6.b and 6.c*) above pH 6.

IV. POSSIBLE APPLICATION OF THE RESULTS

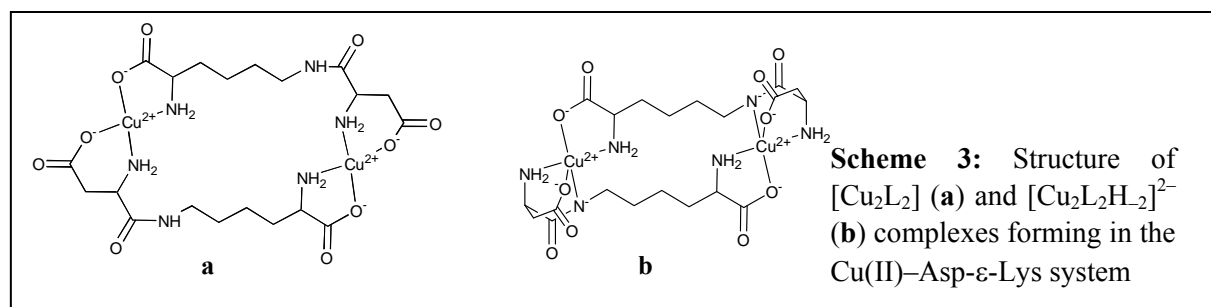
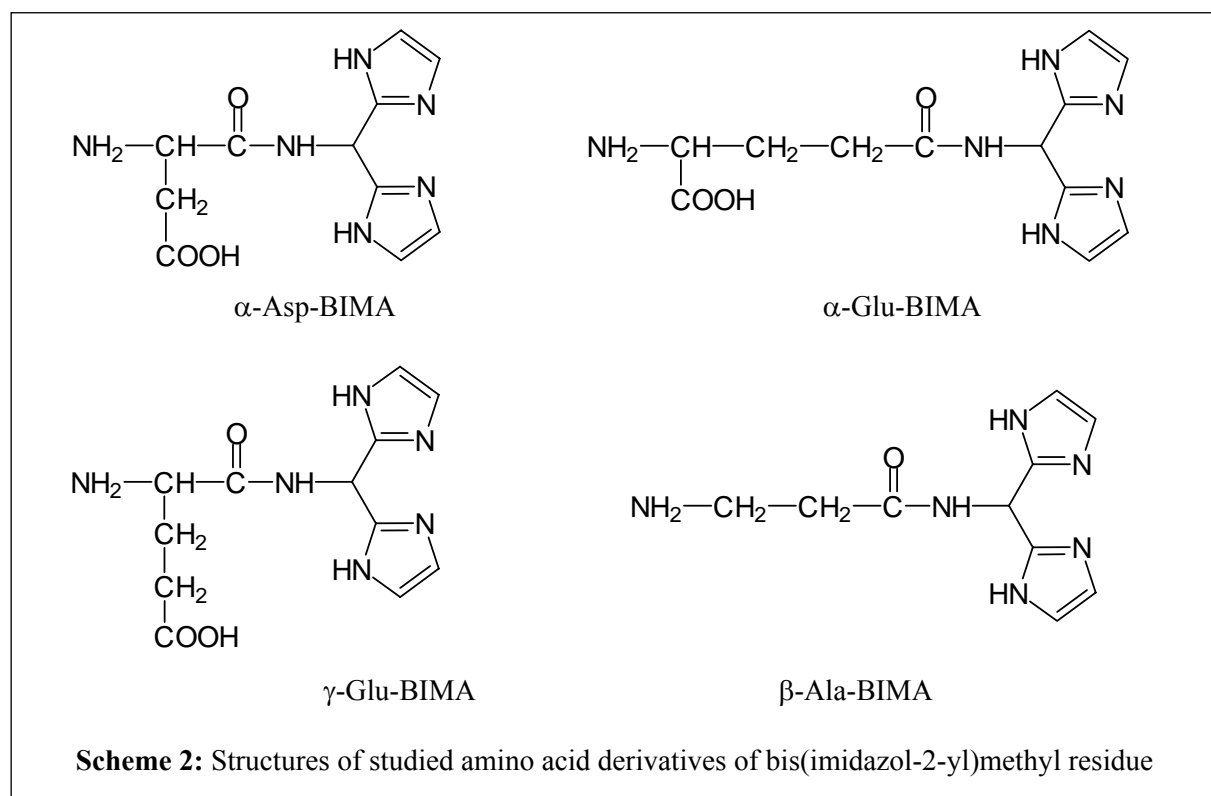
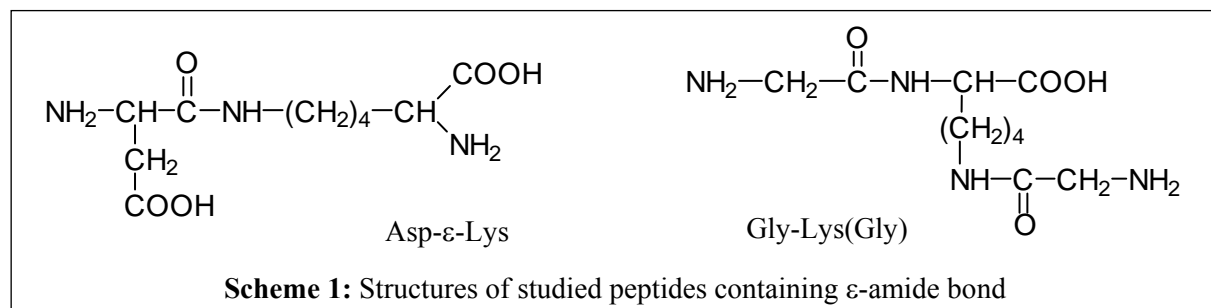
The main goal of this work was to reveal the interaction between some transition metal ions and amino acid and peptides derivatives. The studied ligands contain carboxylate and/or imidazole groups in their side chains, which are the main binding sites of metalloenzymes.

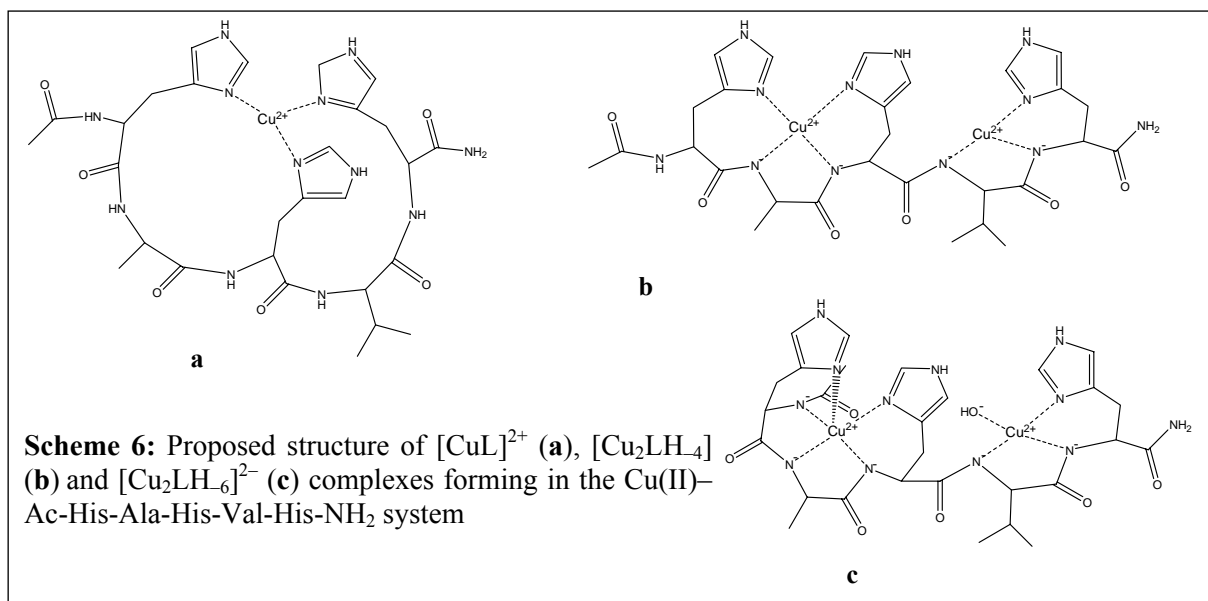
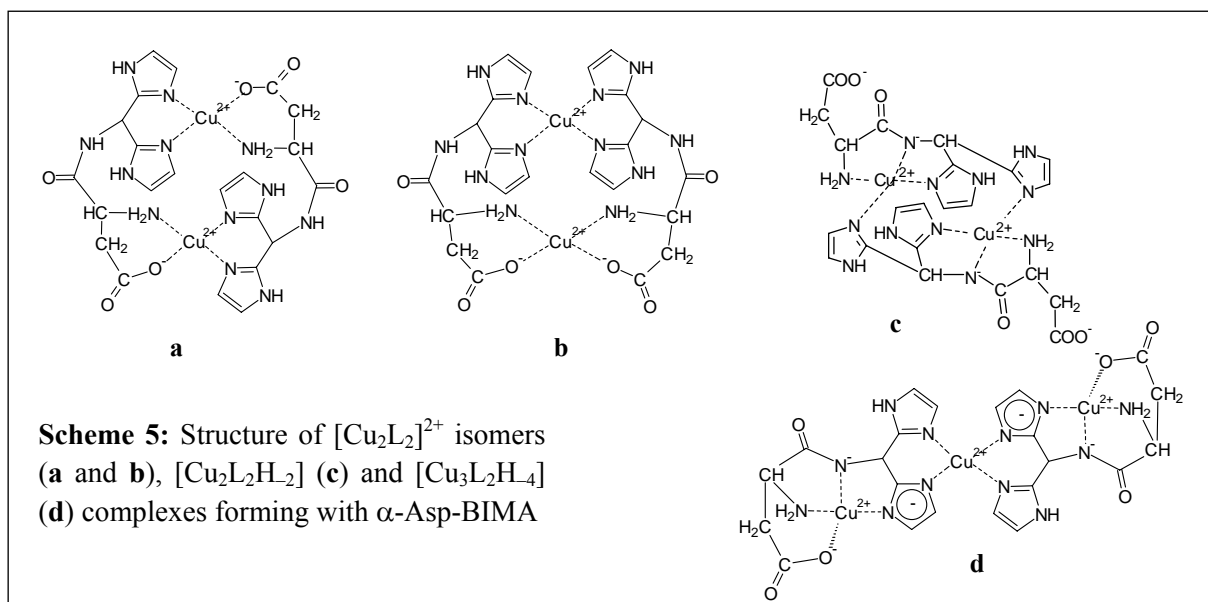
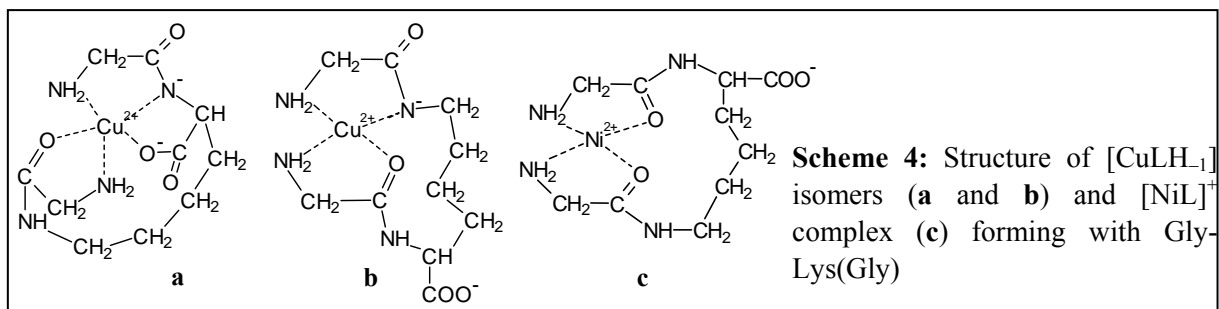
For the bis(imidazol-2-yl) derivatives trinuclear species form, in which the coordination sphere of copper(II) ions with negatively charged imidazolato bridges resembles the active site of Cu,Zn-SOD enzyme. In these complexes the deprotonation of the pyrrole type nitrogens occur at unusually low pH, around the physiological pH range. Therefore these ligands are very promising models for the superoxide dismutase enzymes.

In the case of the histidine containing peptides we also tried to mimic the interaction between metal ions and the peptide chain in the active site of the enzyme. Macrochelates with distorted structure form with these ligands, which structures are found also at the metal

binding site of the enzyme. These binding modes result in higher stability, and the formation of these complexes are shifted to higher pH range.

The presented results are basic research. However, detailed information contributes to understanding the interaction between metal ions and proteins.





V. PUBLICATIONS

Articles connected to the thesis

1. Csilla Kállay, Katalin Várnagy, Imre Sóvágó, Daniele Sanna and Giovanni Micera
Potentiometric and spectroscopic studies on the transition metal complexes of GlyLys(Gly) and Asp- ϵ -Lys
J. Chem. Soc., Dalton Trans. (2002) 92.
2. Katalin Várnagy, Katalin Ösz, Csilla Kállay and Imre Sóvágó
The effect of side chain donor groups on the coordination ability of the bis(imidazol-2-yl) ligands
Prog. Coord. Bioinorg. Chem., **6** (2003) 95.
3. Csilla Kállay, Manuela Cattari, Daniele Sanna, Katalin Várnagy, Helga Süli-Vargha, Imre Sóvágó and Giovanni Micera
Copper(II) complexes of amino acid derivatives of bis(imidazol-2-yl)methyl residue
New J. Chem., **28** (2004) 727.
4. Katalin Ösz, Gábor Lente, Csilla Kállay
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5. Csilla Kállay, Imre Sóvágó, Katalin Várnagy, Daniele Sanna and Manuela Cattari
Transition metal complexes of oligopeptides containing aspartic and/or glutamic acid residues
J. Inorg. Biochem. **99** (2005) 1514–1525.

Article not detailed in the thesis

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Copper(II) complexes of N-terminal protected tri- and tetrapeptides containing histidine residues
J. Chem. Soc., Dalton Trans. (2004) 2702.

Lectures

1. Csilla Kállay
Aszparaginsavat és lizint tartalmazó peptidek átmenetifém-komplexei (Transition metal complexes of peptides containing aspartic acid and lysine)
XXV. OTDK, Kémiai és Vegyipari Szekció, Koordinációs Kémiai Alszekció (Conference for Undergraduate Researchers, Chemistry and Chemical Engineering Section, Coordination Chemistry Group), 10-12 April 2001, Gödöllő, Hungary
2. Katalin Várnagy, Katalin Ösz, Csilla Kállay, Imre Sóvágó and Helga Süli-Vargha
Oldalláncbéli donorcsoportok hatása a bisz(imidazolil) származékok komplexképző sajátosságaira (The effects of side chain donor groups on the complexation of bis(imidazol-2-yl) derivatives)
XXXVII. Komplexkémiai Kollokvium (Colloquium on Coordination Chemistry), 29-31 May 2002, Mátraháza, Hungary
3. Csilla Kállay and Katalin Várnagy
Oldalláncban karboxilcsoportot tartalmazó aminosavak bisz(2-imidazolil)-metil-származékainak átmenetifém-komplexei (Transition metal complexes of amino acid derivatives containing bis(imidazol-2-yl)methyl residues and carboxylic side chains)
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4. Katalin Várnagy, Katalin Ösz, Csilla Kállay and Imre Sóvágó
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5. Csilla Kállay, Imre Sóvágó and Katalin Várnagy
Aszparaginsav- és/vagy glutaminsav-tartalmú oligopeptidek átmenetifém-komplexei (Transition Metal Complexes of Oligopeptides Containing Aspartic and/or Glutamic Acid Residues)
XXXIX. Komplexkémiai Kollokvium (Colloquium on Coordination Chemistry), 26-28 May 2004, Agárd-Gárdony, Hungary
6. Katalin Várnagy, Katalin Ósz, Csilla Kállay and Imre Sóvágó
Coordination chemistry of amino acid and peptide derivatives containing bis(imidazol-2-yl)methyl residue
XXXVIth International Conference on Coordination Chemistry, 18-23 June 2004, Merida, Mexico
7. Imre Sóvágó, Katalin Ósz, Zoltán Nagy, Csilla Kállay, Viktória Rigó, Daniele Sanna, Giovanni Micera, Giuseppe Pappalardo and Enrico Rizzarelli
Copper(II) complexes of peptides of histidine. Models of the binding sites of the enzyme CuZn-SOD and prion proteins
7th European Biological Inorganic Chemistry Conference, 29 Augustus-2 September 2004, Garmisch-Partenkirchen, Germany (Book of Abstracts, p. 49)
8. Viktória Rigó, Csilla Kállay and Imre Sóvágó
A Cu,Zn – SOD enzim aktív centrumának modellezésére alkalmas hisztidintartalmú peptidek Cu(II)komplexeinek oldategyensúlyi vizsgálata (Solution equilibria of copper(II)complexes of peptides containing histidine residues for modelling the active sites of Cu,Zn – SOD enzymes)
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9. Viktória Rigó, Csilla Kállay and Imre Sóvágó
A Cu,Zn – SOD enzim aktív centrumának modellezésére alkalmas hisztidintartalmú peptidek Cu(II)komplexeinek oldategyensúlyi vizsgálata (Solution equilibria of copper(II)complexes of peptides containing histidine residues for modelling the active sites of Cu,Zn – SOD enzymes)
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10. Katalin Várnagy, Ósz Katalin, Csilla Kállay and Süli-Vargha Helga
Bisz(imidazol-2-il) csoportot tartamazó aminosav- es peptidszármazékok komplexképző sajátságai (Coordination chemistry of amino acid and peptide derivatives containing bis(imidazol-2-yl)methyl residue)
XLth. Komplexkémiai Kollokvium (Colloquium on Coordination Chemistry), 18-20 May 2005, Dobogókő, Hungary
11. Csilla Kállay, Katalin Várnagy, Imre Sóvágó, Gerasimos Malandrinos and Nick Hadjiliadis
Copper(II) complexes of pentapeptides related to the active site of Cu,Zn-Superoxide dismutase
20th International Conference on Coordination and Bioinorganic Chemistry, June 5-10 2005, Smolenice, Slovakia (Book of Abstracts, p. 54)

Posters

1. Imre Sóvágó, Csilla Kállay, Katalin Várnagy, Giovanni Micera and Daniele Sanna
Transition metal complexes of oligopeptides containing ϵ -amide bond
10th International Conference on Bioinorganic Chemistry, 26-31 August 2001, Firenze, Italy
J. Inorg. Biochem., **2001**, 86, 439.
2. Katalin Várnagy, Katalin Ösz, Csilla Kállay, Imre Sóvágó, Helga Süli-Vargha, Giovanni Micera and Daniele Sanna
The effects of side chain donor groups on the complexation of amino acid and peptide derivatives containing bis(imidazol-2-yl) group
XXXVth International Conference on Coordination Chemistry, 21-26 July 2002, Heidelberg, Germany (Book of Abstracts, p. 366).
3. Csilla Kállay, Katalin Várnagy, Helga Süli-Vargha, Daniele Sanna and Giovanni Micera
The effect of carboxylate group on the complexation of amino acid derivatives of bis(imidazol-2-yl) group
28th International Conference on Solution Chemistry, 23-28 August 2003, Debrecen, Hungary (Book of Abstracts, p. 208).
4. Csilla Kállay, Katalin Várnagy, Helga Süli-Vargha, Daniele Sanna and Giovanni Micera
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IXth International Symposium on Inorganic Biochemistry, 4-7 September 2003, Szklarska Poręba, Poland (Book of Abstracts, p. 56).
5. Csilla Kállay, Katalin Várnagy, Helga Süli-Vargha, Daniele Sanna and Giovanni Micera
The effect of carboxylate group on the complexation of amino acid derivatives of bis(imidazol-2-yl) group
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6. Csilla Kállay, Manuela Cattari, Daniele Sanna, Imre Sóvágó, Katalin Várnagy and Giovanni Micera
Transition metal complexes of oligopeptides containing aspartic and/or glutamic acid residues
7th European Biological Inorganic Chemistry Conference, 29 August-2 September, Garmisch-Partenkirchen, Germany (Book of Abstracts, p. 197).
7. Katalin Ösz, Gábor Lente and Csilla Kállay
New method of calculating protonation microequilibrium constants and its use for some bis(imidazolyl)methyl derivatives
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8. Katalin Várnagy, Katalin Ösz, Csilla Kállay, Olga Szilágyi, Manuele Cattari, Daniele Sanna, Imre Sóvágó and Giovanni Micera
Coordination chemistry of amino acid and peptide derivatives containing bis(imidazol-2-yl)methyl residue
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9. Katalin Várnagy, Csilla Kállay and Daniele Sanna
Solution equilibria of copper(II) complexes of ligands containing aspartic acid
29th International Conference on Solution Chemistry, 21-25 August 2005, Portorož, Slovenia (Book of Abstracts, p. 200).
10. Katalin Várnagy, Csilla Kállay and Daniele Sanna
Solution equilibria of copper(II) complexes of ligands containing aspartic acid
Xth International Symposium on Bioinorganic Chemistry, 20-25 September 2005, Szklarska Poręba, Poland (Book of Abstracts, p. 108).