

Results of the PhD thesis

---

**OXOVANADIUM PROMOTED AMIDE NITROGEN DEPROTONATION**

Tamás Jakusch

Supervisor:  
Dr. Tamás Kiss

Department of Analytical Chemistry  
University of Szeged

Szeged  
2004

## INTRODUCTION

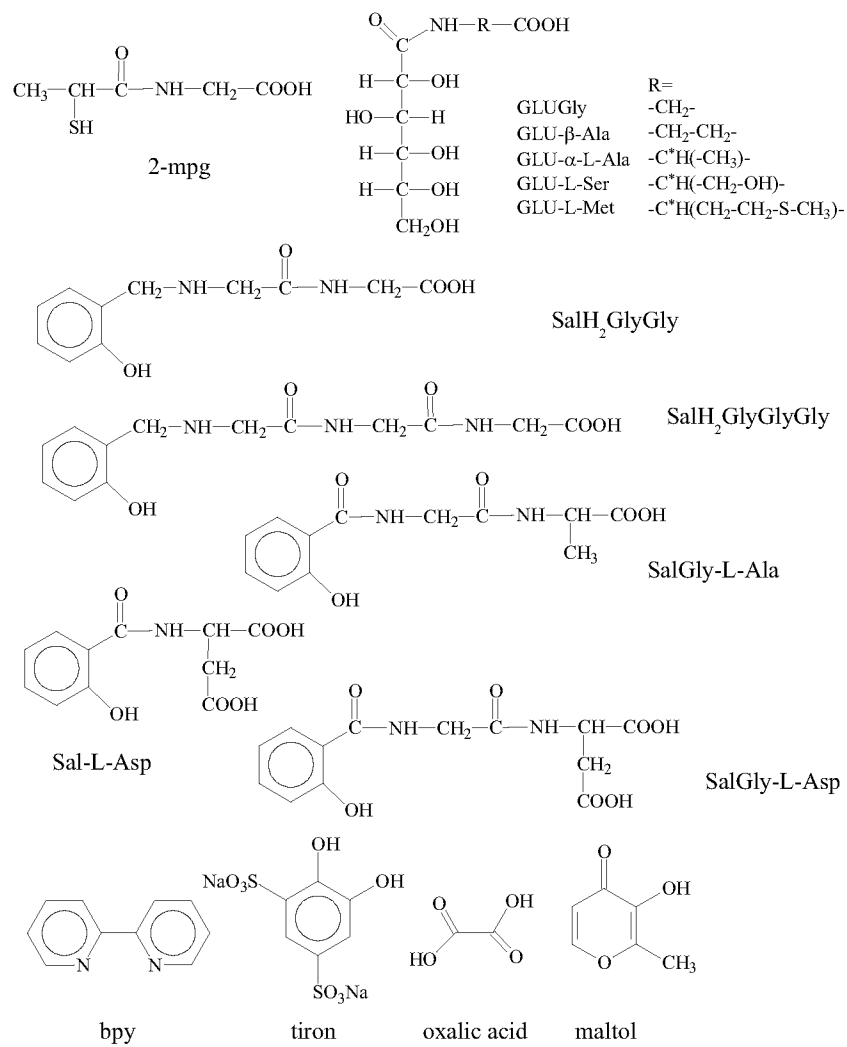
The most questions about the interaction of oligopeptides with the most common bivalent metal ions (*e.g.* Cu<sup>II</sup>, Ni<sup>II</sup>, Pd<sup>II</sup>, Co<sup>II</sup>, Zn<sup>II</sup>) have been answered in the 70s-80s. Perhaps, the most important conclusion of these works was that a primary anchor donor is necessary for the metal ion promoted amide nitrogen deprotonation. The interest of bioinorganic chemists towards oxovanadium(IV) started to grow only in the 90s, and, for this reason, this ion was left out from most of the studies. Therefore, the field of oxovanadium(IV) – peptide interactions – in particular, the V<sup>IV</sup>O promoted deprotonation of amide nitrogens remained largely unexplored.

In the case of the di- and tripeptides with noncoordinating side chains the V<sup>IV</sup>O hydroxide precipitates from the solution. Some complexes with deprotonated amide nitrogen of dipeptides can only be detected at very high ligand excess and pH > 7.5 by using CD and EPR spectroscopies. It was also shown, that amine group (as opposed to other metal ions, like as Cu<sup>II</sup>, Ni<sup>II</sup>, Co<sup>II</sup>, Pd<sup>II</sup>) is not a suitable anchor for the oxovanadium(IV) promoted amide nitrogen deprotonation. The first X-ray structures of complexes containing deprotonated amide nitrogen were published in the beginning of the 90s. The first single crystal structures of some ternary complexes with biologically relevant ligands – simple dipeptides – were published in 1998. The article with the first pieces of evidence of V<sup>IV</sup>O promoted amide nitrogen deprotonation in aqueous solution at about pH 4.5 was presented in the same year. The ligand was salicylglycine, in which the phenolate seemed to be the anchor.

During our work we aimed at collecting data on the V<sup>IV</sup>O-amide nitrogen interactions. Accordingly, the goals of our studies were:

- Searching for ligands, suitable of keeping V<sup>IV</sup>O in aqueous solution, preventing from the hydrolysis of V<sup>IV</sup>O via the active contribution of the coordination of the amide nitrogen(s).
- Studying the effect of the second ligand on the amide nitrogen deprotonation in ternary systems. (*e.g.*, V<sup>IV</sup>O + two ligands).
- Determining the stability constant and the species distribution of the V<sup>IV</sup>O complexes of the ligands chosen.

–



- Characterising the  $V^{IV}O$  complexes formed in our system by using a range of complementary experimental techniques.
- Based on the stoichiometry, the stability constants and the spectral behaviour, determining the binding mode of the  $V^{IV}O$  species, especially those containing deprotonated amide nitrogen(s).

The oxovanadium(IV) binding capability in aqueous solution and the metal ion induced amide nitrogen deprotonation in a range of ligands (more than ten) was examined by pH-metry, EPR-, VIS- and when applicable CD-spectroscopic methods.

All ligands studied contain terminal carboxylic group and can be classified in four major groups:

1. A dipeptide derivative containing thiolate group: *N*-(*S,R*)-2-mercapto-propionyl-glycine: 2-mpg.
2. Pseudodipeptides containing more than one aliphatic hydroxyl groups, *N*-D-Gluconilamino acids: GLUGly, GLU-L-Ser, GLU- $\alpha$ -Ala, GLU- $\beta$ -L-Ala, GLU-Met.
3. Reduced Schiff-base derivatives of GlyGly and GlyGlyGly with salicylaldehyde: SalH<sub>2</sub>GlyGly, SalH<sub>2</sub>GlyGlyGly.
4. Peptide derivatives of salicylic acid
  - a, Pseudotriptides: SalGly-L-Ala, SalGly-L-Asp.
  - b, Oligopeptides with aspartic acid moiety: Sal-L-Asp, SalGly-L-Asp.

Ternary systems with  $V^{IV}O$ -2-mpg-B were also studied, where the B stands for: *N*-2,2'-bipyridil, tiron, maltol and oxalic acid.

## EXPERIMENTAL

The acid-base properties and the stability constants of the  $V^{IV}O$  complexes of the ligands were studied by pH-potentiometry at 25 °C-on 0.20 M ionic strength (KCl). The titration were carried out with computer controlled system. The results were evaluated by using the suites of computer programs of PSEQUAD and SUPERQUAD.

The EPR spectra were usually recorded at liquid nitrogen temperature. The spectra were simulated and EPR parameters were determined with a suitable computer program. The binding mode of the complexes were determined by comparing of the observed and estimated parallel coupling constants of the suggested structure, using an empirical equation published by Chasteen. When it was possible, the information obtained from the CD and UV-VIS spectra were also utilised.

## RESULTS

The conclusions obtained from the various systems can be summarised as follows:

1. In the 2-mpg system at 1:10 metal to ligand ratio the hydrolysis of the  $V^{IV}O$  was found to be negligible. pH-potentiometric measurements and the EPR spectra proved that the thiolate group of the 2-mpg ligand together with the carboxylate moiety serves as a suitable primary anchor for oxovanadium(IV) promoted amide nitrogen deprotonation. Coordination of the thiolate and the deprotonated amide nitrogen occurs in a single step, resulting a 5+5 membered joint chelate ring system. The position of the thiolate groups plays an important role in the oxovanadium(IV) promoted amide nitrogen deprotonation.
2. Based on the behaviour of the ternary systems studied, it can be concluded that the neutral B ligand like bpy (which contains N donors with empty  $\pi$  orbitals, and capable of back coordination) promotes the deprotonation of the amide nitrogen through enhanced ternary complex formation. On the other hand, ligands such as tiron, maltol or oxalate, with negatively charged O donors, increase the electron density on the metal ion and therefore make the ternary complex formation unfavoured.
3. From the pH-metric measurements at  $M:L = 1:5$  the hydrolysis of the  $V^{IV}O$  was found to be negligible with all gluconylamino acid. In the pH 4-5 region

two moles extra base consumption per mole of oxovanadium(IV) is seen on the titration curves. The alcoholate – together with the already coordinated carboxylate and possible with non deprotonated alcoholic-OH groups – serve as an anchor for the  $V^{IV}O$  promoted amide nitrogen deprotonation. The loss of the alcoholic and amide proton occurs almost as a single step resulting an EPR silent oligonuclear species (probably a dimer). With the increasing pH one more alcoholate coordinates to each of the two vanadium centers in the dimeric complex. At pH > 10, due to the next deprotonation step, the dimer – in while the coordination sphere of the  $V^{IV}O$  was already complete – breaks up to EPR active monomers. However the CD spectra of these system clearly show, that the amide nitrogen remains coordinated to the metal ion in these monomers.

4. The  $V^{IV}O$  complexes of  $SalH_2GlyGly$  and  $SalH_2GlyGlyGly$  ligands were possible to study with pH-metric method at the pH range of 2-8 at  $L:M \geq 2$ .  $V^{IV}OLH_1$  complex containing coordinated amide nitrogen (the pK of the process is 5,43) was possible to detect only for the tripeptide analogue. As the EPR was unable to differentiate between the  $V^{IV}OL_2$  complexes of the two ligands, the structure of them is expected to be identical. Based on the measured and the estimated perpendicular coupling constants of  $V^{IV}OL_2$  and  $V^{IV}OLH_1$  species it can be concluded that one phenolate or one amine-N is coordinated in axial position in both cases.

The difference in the behaviour of these two pseudopeptides demonstrates that the coordination of the carboxylate group in the appropriate position is an important parameter for the oxovanadium(IV) promoted amide nitrogen deprotonation. It is possible only in the case of  $SalH_2GlyGly$  for carboxylate, amide nitrogen, phenolate and amino-N to form a 6+5+5 membered joint chelate ring system, where the amide nitrogen is a member of two rings at the same time.

5. During the pH-potentiometric measurements of  $V^{IV}O$ - $SalGly$ -L-Ala system the precipitation of the  $V^{IV}O(OH)_2$  was not observed at  $L : M \geq 2$ . The titration curves were fitted satisfactorily with assuming only  $MLH_x$  species but in 5-7 pH region where slow reactions occurred the difference between the calculated and observed titration curves was found to be relatively high. The results of the pH-metric- EPR- (performed both at room and at liquid nitrogen temperature).

UV-VIS- and CD-spectroscopic measurements allowed us to conclude that in the pH range of 5-6 (in parallel with slow hydrolytic processes)  $V^{IV}O$  promoted amide nitrogen deprotonation takes place, resulting in a  $V^{IV}OLH_2$  species. The EPR spectra of this complex detected in frozen sample is significantly different from signal of the  $V^{IV}OLH_1$  type SalGly species. The difference between the parallel coupling constants is approximately equal to the effect, which would be resulted by an amide nitrogen coordination. This is the first detection of a significant amount of a  $V^{IV}O$  complex formed in aqueous solution, which contains two deprotonated amide nitrogens in the coordination sphere. The coordination of the amide nitrogens from all experimental techniques occurs as almost in a single step in contrast to the consecutive deprotonation of the  $Cu^{II}$  dipeptide complexes with analogous coordination mode. The overall pK of the amide nitrogen calculated from the RT-EPR measurements was found to be 5.31, which is in a good agreement with the results obtained from pH-potentiometric measurements. ( $\Sigma pK/2 = 5.37$ ).

6. The analogous behaviour (*i.e.*, similar pK values and almost identical EPR spectra) of the SalGly- and Sal-L-Asp –  $V^{IV}O$  systems indicates that the coordination of the extra carbocylate group is axial. The different pK-s and EPR parameters of the tripeptide analogues suggest not identical coordination mode in the  $V^{IV}OL$  complexes in the two pseudopeptides. The equatorial coordination of the aspartate moiety could be a possible explanation.

The  $V^{IV}O$  is able to promote the deprotonation of the amide nitrogen in both cases like in the non-Asp derivatives, however the extra carboxylate group exerts two different effects. In the case of Sal-L-Asp the axial coordination of the aspartate has no effect on the deprotonation of the amide nitrogen: the corresponding pK is the same as for SalGly.

As the extra carbocylate group of the SalGly-L-Asp is equatorially coordinated in the  $V^{IV}OL$  complex, a rearrangement of the donor groups is necessary for the formation of  $V^{IV}OLH_2$  complex of SalGly-L-Ala type. For the Asp derivative, the average of the pK-s of cooperative deprotonation of the amide nitrogens is higher by 0.6 log unit than for SalGly-L-Ala. For both tripeptide analogues (SalGly-L-Ala, SalGly-L-Asp) the maximum amount of the

$V^{IV}OLH_{-1}$  complex remains uncertain, as the various experimental techniques yielded different results.

General conclusions:

7. The deprotonation and the coordination of  $V^{IV}O$  to the peptide amide group - except for  $SalH_2GlyGlyGly$  - was confirmed in all system studied by at least two independent methods (*e.g.*, pH-metry- and EPR- or CD-spectroscopy). For ligands containing one nitrogen atom - 2-mpg, *Sal-L-Asp*, *N-D-gluconylamino* acids and *SalGly* - the deprotonation of the amide nitrogen occurs at the pH 4-5. The amide nitrogen deprotonation of the ligands with two nitrogen atoms  $SalH_2GlyGly$  and  $SalGly-L-Ala$  - is promoted by  $V^{IV}O$ , and the pK is almost one unit higher.

8. Based on the results from the  $SalH_2GlyGly$ -,  $SalH_2GlyGlyGly$  - and  $SalGly-L-Ala - V^{IV}O$  systems it seems reasonable to conclude that in acidic pH the oxovanadium(IV) promoted amide nitrogen deprotonation typically happened in systems where more than one anchor already coordinated to the metal ion, and where the deprotonation of the amide nitrogen or nitrogens results in the formation of joint three or four chelate ring, and where the amide nitrogen is supposed to be a member of at least two rings. This conclusion is further supported by the observation that  $V^{IV}O(AH_{-1})_2$  type complex containing two amide nitrogens, where one anchor is sufficient for the metal ion promoted amide deprotonation was not identified in any of the examined systems.

9. When donors phenolate, thiolate, alcoholate + alcoholic-OH-s, which serve as anchors together with the carbocylate group are compared, it can be concluded that the phenolate containing ligands form more stabile  $V^{IV}OL$  complexes than the thiolate or alcoholate containing pseudopeptides. This way phenolates act as stronger anchors to keep the oxovanadium(IV) in solution. The pK of the  $V^{IV}O$  promoted amide nitrogen deprotonation increases in the order of thiolate < alcoholate < phenolate. The preferred oxygen coordination of the oxovanadium(IV) increases the local charge of the metal centre inhibiting the deprotonation of the amide nitrogen.

10. The proposed binding modes make it possible to estimate a more correct value for the contribution of the amide nitrogen to the parallel coupling constant. The values derived from individual cases are in a relatively broad range  $35.5\text{-}40.0 \times 10^{-4} \text{cm}^{-1}$ , and depend on the total charge of the coordinated donors. Donors with charge of -3 have a contribution of  $35.5\text{-}38.0 \times 10^{-4} \text{cm}^{-1}$  and donors with charge of -4 the contribution is in the range  $38.0\text{-}40.0 \times 10^{-4} \text{cm}^{-1}$ .

## PUBLICATIONS

### List of the publications the thesis based on

1. **Tamás Jakusch**, Ágnes Dörnyei, Isabel Correia, Lígia M. Rodrigues,; Gábor K. Tóth, Tamás Kiss, João Pessoa, Susana Marcão: *Interaction of  $V^{VO}$ ,  $V^{VO}_2$  and  $Cu^{II}$  with a peptide analogue SalGly-L-Ala*. European Journal of Inorganic Chemistry (11) (2003) 2113-2122. IF.: 2,526
2. Tamás Kiss, **Tamás Jakusch**, João Costa Pessoa Pessoa, Ana Isabel Tomaz: *Interactions of VO(IV) with oligopeptides*. Coordination Chemistry Reviews 237(1-2) (2003) 123-133. IF.: 5,853
3. João Costa Pessoa, Isabel Correia, Tamás Kiss, **Tamás Jakusch**, Margarida M.C.A. Castro, Carlos F.G.C. Geraldes: *Oxovanadium(IV and V) and copper(II) complexes of N-salicyl-glycylglycine and N-salicyl-glycylglycylglycine*. Journal of the Chemical Society, Dalton Transactions (23) (2002) 4440-4450.  
IF.: 3,023
4. **Tamás Jakusch**, Péter Buglyó, Ana Isabel Tomaz, João Costa Pessoa, Tamás Kiss: *Thiolate-S as anchoring donor in the binary and ternary VO (IV) complexes of mercaptopropionylglycine*. Inorganica Chimica Acta 339 (2002) 119-128.  
IF.: 1,566
5. Béla Gyurcsik, **Tamás Jakusch**, Tamás; Kiss: *Oxovanadium(IV) complexes of N-D-gluconylamino acids*. Journal of the Chemical Society, Dalton Transactions (7) (2001), 1053-1057. IF.: 2,820

6. **Tamás Jakusch**, Susana Marcão, Ágnes Dörnyei, Lília Rodrigues, Isabel Correia, Joao Costa Pessoa\*, Tamás Kiss: *Oxovanadium(IV) complexes of Salicyl-L-Aspartic Acid and Salicyl-Glycyl-L-Aspartic Acid* (Előkészületben lévő közlemény)

ΣIF: 15,788

#### Other publications:

1. Tamás Kiss, **Tamás Jakusch**: *Idea and newest achievements in medicinal bioinorganic chemistry*. Magyar Kémikusok Lapja 59(9) (2004), 311-320.
2. Valerio Di Marco, Melinda Kilyén, **Tamás Jakusch**, Péter Forgó, György Dombi,; Tamás Kiss.: *Complexation properties of ethylenediaminetetramethylenephosphonic acid (EDTMP) with Al<sup>III</sup> and V<sup>VO</sup>*. European Journal of Inorganic Chemistry (12) (2004) 2524-2532.
3. Ágnes Dörnyei, Eugenio Garribba, **Tamás Jakusch**, Péter Forgó, Giovanni Micera, Tamás Kiss: *Vanadium(IV,V) complexes of d-saccharic and mucic acids in aqueous solution*. Dalton Transactions (12) (2004) 1882-1891
4. Isabel Correia, João Costa Pessoa, M. Teresa Duarte, Rui T. Henriques,; M. Fatima M. Piedade, Luis F. Veiros, **Tamás Jakusch**, Tamás Kiss, Ágnes Dörnyei, M. Margarida C. A. Castro, Carlos F.G.C. Geraldes, Fernando Avecilla: *N,N'-ethylenebis(pyridoxylideneiminato) and N,N'-ethylenebis(pyridoxylaminato): Synthesis, characterization, potentiometric, spectroscopic, and DFT studies of their vanadium(IV) and vanadium(V) complexes*. Chemistry--A European Journal 10(9) (2004) 2301-2317.
5. Erzsébet Kiss, Kenji Kawabe, Asuka Tamura, **Tamás Jakusch**, Hiromu Sakurai, Tamás Kiss: *Chemical speciation of insulinomimetic VO(IV) complexes of pyridine-N-oxide derivatives: binary and ternary systems*. Journal of Inorganic Biochemistry 95(2-3) (2003) 69-76.
6. **Tamás Jakusch**, Wenzheng Jin, Luqin Yang, Tamás Kiss, Debbie C. Crans: *Vanadium(IV/V) speciation of pyridine-2,6-dicarboxylic acid and 4-hydroxy-pyridine-2,6-dicarboxylic acid complexes: potentiometry, EPR spectroscopy and comparison across oxidation states*. Journal of Inorganic

Biochemistry 95(1) (2003) 1-13.

7. N. Kotsakis, C. P. Raptopoulou, V. Tangoulis, A. Terzis, J. Giapintzakis, **T. Jakusch**, T. Kiss, A. Salifoglou: *Correlations of Synthetic, Spectroscopic, Structural, and Speciation Studies in the Biologically Relevant Cobalt(II)-Citrate System: The Tale of the First Aqueous Dinuclear Cobalt(II)-Citrate Complex*. Inorganic Chemistry (2003), 42(1), 22-31.
8. Debbie C. Crans, A. Raza Khan, Mohammed Mahroof-Tahir; Sujit Mondal, Susie M. Miller, Agnete la Cour, Oren P. Anderson, **Tamás Jakusch**, Tamás Kiss: *Bis(acetylamido)oxovanadium(IV) complexes: solid state and solution studies*. Journal of the Chemical Society, Dalton Transactions (22) (2001) 3337-3345.
9. D. Hollender, **T. Jakusch**, S. Buhsina, A. Aboukais, E. Abi Aad, T. Kiss: *Copper(II) and oxovanadium(IV) complexes of d-3-phosphoglyceric acid*. Journal of Inorganic Biochemistry 85(4) (2001) 245-251.
10. Tamás Kiss, **Tamás Jakusch**, Melinda Kilyén, Erzsébet Kiss, Andrea Lakatos: *Speciation of bioactive Al(III) and VO(IV) complexes in biological systems*. Acta Pharmaceutica Hungarica (2000), 70(3-6), 175-186.
11. Tamás Kiss, **Tamás Jakusch**, Melinda Kilyén, Erzsébet Kiss, Andrea Lakatos: *Speciation of bioactive Al(III) and VO(IV) complexes in biological systems*. Polyhedron 19(24-25) (2000) 2389-2401.
12. Debbie C. Crans, Luqin Yang, **Tamás Jakusch**, Kiss, Tamas: *Aqueous Chemistry of Ammonium (Dipicolinato)oxovanadate(V): The First Organic Vanadium(V) Insulin-Mimetic Compound*. Inorganic Chemistry 39(20) (2000) 4409-4416.
13. T. Gajda, B. Gyurcsik, **T. Jakusch**, K. Burger, B. Henry, J.-J. Delpuech: *Coordination chemistry of polyhydroxy acids: role of the hydroxy groups*. Inorganica Chimica Acta 275-276(1,2) (1998) 130-140.

#### Lectures and posters:

1. B. Gyurcsik, **T. Jakusch**, L. Nagy, K. Burger: Transition metal complexes of N-D-gluconylglycyl glycine, 1st COST European workshop on

biocoordination Chemistry, Budapest, Hungary September 5-6, 1994 (poszter)

2. B. Gyuresik, **T. Jakusch**: Equilibrium and solution structural study of oxovanadium(IV)<sup>2+</sup> ions with some carbohydrate derivatives, 33th ICC "The Chemistry of Metal Ions in Everyday Life", Firenze, Italy, August 30-September 4, 1998 (poszter)
3. B. Gyuresik, **T. Jakusch**, T. Kiss: Equilibrium and solution structural study of oxovanadium(IV)<sup>2+</sup> ions with some *N*-D-gluconylamino acids, COST D8 and ESF-Workshop on Biological and Medicinal Aspects of Metal Ion Speciation, Szeged, Hungary, August 22-25, 1998 (poszter)
4. **T. Jakusch**, P. Buglyó és T. Kiss, Vanadium Complexes of Salicylglycine and Salicylglycylalanine in Aqueous Solution, Microsymposium of Biological Aspects of Vanadium Chemistry-Chemistry, Biochemistry and Therapeutic Application of Vanadium Compounds, 37th IUPAC Congress 27th GDCh General Meeting, Berlin, Germany, August 14-19, 1999 (poszter)
5. **T. Jakusch**, A. I. Tomaz, P. Buglyó, J. Costa Pessoa and Tamás Kiss: The role of tiolate in the oxovanadium(IV) induced peptide amide deprotonation, 5th European Biological Inorganic Chemistry Conference, Toulouse, July 17-20, 2000 (poszter)
6. **T. Jakusch**, A. I. Tomaz, E. Kiss, P. Buglyó, J. Costa Pessoa and T. Kiss: VO(IV)-glutathione and related systems, International Symposium "Metals in environmental Medicine" COST Symposium Lectures, Wroclaw, October 18-21, 2000 (előadás)
7. T. Kiss T, E. Kiss, **T. Jakusch**, S. Bouhsina, G. Micera: Biospeciation of Insulin-mimetic VO(IV) compounds in blood serum, *Journal of Inorganic Biochemistry*, **86**, 62 - 62, 2001, 10th International Conference on Bioinorganic Chemistry, Florence, Italy, August 26-31, 2001 (poszter)
8. I. Correia, J. Costa Pessoa, T. Kiss, **T. Jakusch**, S. Marcao, A. I. Tomaz, L. Rodrigues: Deprotonation and coordination to oxovanadium(IV) and copper(II) of two dipeptide amide nitrogen atoms. A potentiometric and spectroscopic study., *Journal of Inorganic Biochemistry*, **86**, 186 - 186, 2001, 10th International Conference on Bioinorganic Chemistry, Florence, Italy, August 26-31, 2001 (poszter)

9. **T. Jakusch**, I. Correia, J. Costa Pessoa, T. Kiss: Oxovanadium(IV) and copper(II) complexes of reduced Schiff-bases, *Journal of Inorganic Biochemistry*, **86**, 278 - 278, 2001, 10th International Conference on Bioinorganic Chemistry, Florance, Italy, August 26-31, 2001 (poszter)
10. **T. Jakusch**, I. Correia, A. Dörnyei, J. Costa Pessoa, T. Kiss,  $V^{IV}O$  and  $V^{VO}_2$  complexes of a Schiff base derivatives of ethylenediamine and pyridoxal, XXXVth International Conference on Coordination Chemistry, Heidelberg, July 21-26, 2002 (poszter)
11. J. Costa Pessoa, I. Correia, **T. Jakusch**, T. Kiss, S. Marcão, L. Rodrigues, The Oxovanadium(IV)-N-Salicyl-L-Aspartic acid system: a potentiometric and spectroscopic study, 6<sup>th</sup> European Biological Inorganic Chemistry Conference, Lund, Sweden - Copenhagen, Denmark, July 29-August 3, 2002 (poszter)
12. J. Costa Pessoa, I. Correia, T. Kiss, **T. Jakusch**, M.M.C.A. Castro, C.F.G.C. Geraldes: New Vanadium complexes with tetradentate ligands derived from the reaction of aromatic o-hydroxyaldehydes and diamines, 6<sup>th</sup> European Biological Inorganic Chemistry Conference, Lund, Sweden - Copenhagen, Denmark July 29-August 3, 2002 (poszter)
13. **Tamás Jakusch**, Saâd Bouhsina, Hiromu Sakurai and Tamás Kiss: Binding Constant of VO(IV) to Transferrin, 28<sup>th</sup> International Conference on Solution Chemistry, Debrecen, Hungary August 23-28 2003 (poszter)
14. João Costa Pessoa, Isabel Correia, Carlos F. G. C. Geraldes, Margarida Castro, **Tamás Jakusch** and Tamás Kiss:  $V^{IV}O$  and  $V^{VO}_2$  complexes of schiff base derivatives of ethylenediamine and vitamine B6, *Journal of Inorganic Biochemistry*, Volume 96, Issue 1, 15 July 2003, Page 211, 11th International Conference on Biological Inorganic Chemistry, Cairns, Australia, 19 July - 23 July 2003
15. **Tamás Jakusch**, Saâd Bouhsina, Hiromu Sakurai and Tamás Kiss: Binding Constant of VO(IV) to Transferrin, The 4<sup>th</sup> International Symposium of Chemistry and Biological Chemistry and Biological Chemistry of Vanadium. 3-5 September, Szeged, Hungary 3 (poszter)
16. **Jakusch Tamás**, Gyurcsik Béla, Kiss Tamás. N-D-Glükonil-aminosavak oxovanádium(IV)<sup>2+</sup> komplexeinek egyensúlyi és oldatszerkezet vizsgálata, XXI. Kémiai Előadói Napok, Szeged 1998. október 26-28

17. **Jakusch Tamás**, Buglyó Péter, Kiss Tamás: Vanádium indukált amid deprotonálódás oligopeptidekben, XXXIV. Komplexkémiai Kollokvium, Tata, 1999 május 19-21.
18. **Jakusch Tamás**, Ana Isabel Tomaz, Buglyó Péter, Joao Costa Pessoa, Kiss Tamás: Fémion indukált amid deprotonálódás VO(IV)-2-merkaptopropionil-glicin komplexekben, 3. Doktori Kémiai Iskola, Mátraháza, 2000. április 10-12
19. **Jakusch Tamás**, Ana Isabel Tomaz, Buglyó Péter, Joao Costa Pessoa, Kiss Tamás: Fémion indukált amid deprotonálódás VO(IV)-2-merkaptopropionil-glicin komplexekben, XXXV. Komplexkémiai Kollokvium, Kecskemét, 2000 május 24-26.
20. **Jakusch Tamás**, Isabel Correia, Joao Costa Pessoa, Kiss Tamás: Redukált Schiff-bázis típusú vegyületek oxovanádium(IV) és Cu(II) komplexei: oldategyensúlyi és spektrális vizsgálatok, XXXVI. Komplexkémiai Kollokvium, Pécs, 2001. május 23-25.
21. **Jakusch Tamás**, Isabel Correia, Dörnyei Ágnes, Joao Costa Pessoa, Kiss Tamás: Piridoxál Schiff-bázis származékok oxovanádium(IV) és dioxovanádium(V) komplexei, XXXVII. Komplexkémiai Kollokvium, Mátraháza, 2002. május 29-31.
22. **Jakusch Tamás**, Kiss Tamás: Az oxovanádium kölcsönhatása transzferrinnel, XXXVIII. Komplexkémiai Kollokvium, Gyula, 2003. május 21-23