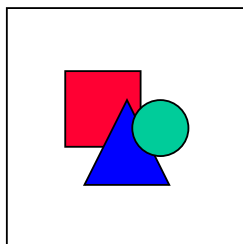


PhD Thesis Abstract



REACTIONS OF THE IRON(III) HYDROXO DIMER WITH  
INORGANIC LIGANDS

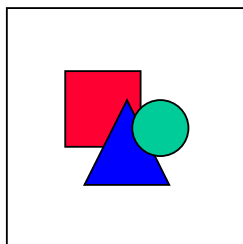
*Gábor Lente*

Supervisor: Dr. István Fábián

University of Debrecen  
Faculty of Science

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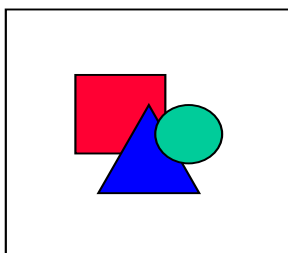
PhD Thesis Abstract



# REACTIONS OF THE IRON(III) HYDROXO DIMER WITH INORGANIC LIGANDS

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## 1. Introduction and research objectives

Iron is the most abundant transition element in the solar system and on the earth. It is the fourth most abundant element in the crustal rocks and is believed to be the main constituent of the core of the earth. In the oxidative atmosphere of our planet iron mostly occurs in the oxidation state of +3. This metal has been known to humankind since ancient times and has had an immense impact on history and culture. Today iron is produced on a vast scale industrially.

Iron is classified as essential in biological systems. It has been a key metal in the evolution of life from primitive bacteria and algae to higher organisms. The major function of the metal in iron-containing proteins is usually promoting some kind of electron transfer or the activation of small molecules, especially dioxygen, which is due to the advantageous redox chemistry of the metal. Iron(III) is often found in biological systems in oxo- or hydroxo-bridged di- or oligonuclear structures. Numerous enzymes with dinuclear iron(III) centers, such as methane monooxygenase, have been described with various functions in living organisms. Structural motifs found in these enzymes can be used to design protein-free dinuclear iron(III) catalysts.

The complexes of iron(II) and iron(III) have played major roles in understanding the mechanisms of substitution and redox processes. Iron(III), like almost all cations with a charge +3 or higher, gives rise to polynuclear species in aqueous solution over a characteristic pH range. It is well established that the mononuclear hydrolytic species are important in the kinetics and mechanism of the substitution and redox reactions, and are often much more reactive than the aqua ion itself. It seems to be quite reasonable that polynuclear hydrolytic complexes may also have similar roles, but this field received much less attention compared to the investigation of mononuclear forms. Reliable information on aqueous dinuclear iron(III) forms and their reactivity patterns could be beneficial for the ongoing studies on the biological role of iron(III) in addition to holding considerable interest for the mechanistic research of inorganic reactions. Studies in this field may shed light on the formation of dinuclear iron(III) cores and contribute to the understanding of the basic kinetic features of di- and multinuclear iron(III) complexes.

The major goal of the present study was to characterize the kinetics and equilibrium of direct ligand substitution reactions of the aqueous iron(III) hydroxo dimer,  $\text{Fe}_2(\cdot\text{-OH})_2(\text{H}_2\text{O})_8^{4+}$ , with

simple inorganic ligands and draw structural and mechanistic conclusions from the results. In order to achieve this goal, it was necessary to identify the inorganic ligands that react with the hydroxo dimer directly. A further objective was to explore the possible role of the iron(III) hydroxo dimer in redox reactions between iron(III) and inorganic species with special emphasis on the iron(III) / sulfur(IV) system because of its outstanding significance.

## 2. Experimental methods

Low chloride iron(III) perchlorate (Aldrich) was used to prepare iron(III) solutions. Other chemicals used in this study were of analytical reagent grade. Doubly deionized, ultrafiltered water was used to prepare solutions.

Equilibrium studies, including the determinations of relevant protonation constants for ligands, were carried out using standard UV-vis spectrophotometric or pH-potentiometric methods. Kinetic measurements were performed with the stopped flow method using an Applied Photophysics SX-18 MV instrument at  $10.0 \pm 0.01$  and  $25.0 \pm 0.01$  °C and ionic strength 1.0 M ( $\text{NaClO}_4$ ). Charge transfer bands of different iron(III) complexes were used for the photometric detection of kinetic measurements.

Equilibrium data were evaluated by the software package *PSEQUAD*, and the software package *SCIENTIST* was used for general fitting purposes. The traditional kinetic evaluation method based on pseudo first-order curves could only be employed in a few cases. In these examples, kinetic parameters were determined by fitting the experimental values of the pseudo first-order rate constant ( $k_{\text{obs}}$ ) based on the explicit formula derived for  $k_{\text{obs}}$ . The rate constants in other systems were calculated by fitting the experimental kinetic traces directly to the simultaneous differential equations defined by the kinetic model with the software packages *SCIENTIST* or *ZiTa*. In a few cases further support for the established kinetic model was obtained by determining the number of absorbing species with matrix rank analysis of time-dependent spectral data carried out using the singular value decomposition method.

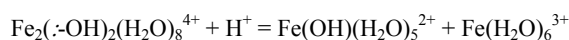
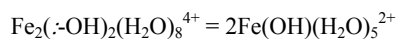
### 3. Results

3.1. *It was established that only the species  $Fe(H_2O)_6^{3+}$ ,  $Fe(OH)(H_2O)_5^{2+}$ , and  $Fe_2(-OH)_2(H_2O)_8^{4+}$  are present at considerable concentration levels in aqueous iron(III) solutions in the reproducibly accessible pH and concentration range.*

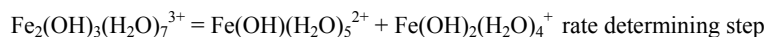
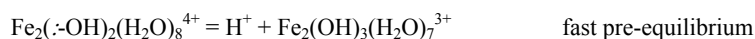
The stability constants for the hydroxo complexes were determined from the spectrophotometric data set and the individual UV-vis spectra of the different iron(III) species were calculated. Matrix rank analysis provided evidence that all spectral data could be sufficiently interpreted considering three absorbing species. It was also necessary to assume the presence of the dihydroxo monocomplex,  $Fe(OH)_2(H_2O)_4^+$ , at very low concentration levels in a few cases to evaluate kinetic data. The stability constant of this species could not be determined by UV-vis spectrophotometry, and an earlier value obtained by pH-potentiometry was used throughout the work.

3.2. *A novel, extended mechanism was proposed to interpret the kinetics of the hydrolytic reactions of iron(III).*

Previous studies proved that the interconversion of the mononuclear forms was diffusion controlled or nearly so. An earlier mechanisms proposed for the decomposition of  $Fe_2(-OH)_2(H_2O)_8^{4+}$  comprised a direct and a proton-assisted pathway:



It was confirmed in this work that a further pathway should be taken into account at higher pH (> 1.8). This pathway is inversely proportional to the hydrogen ion concentration and is interpreted as a rapid proton loss from the hydroxo dimer followed by decomposition:



The putative complex  $Fe_2(OH)_3(H_2O)_7^{3+}$  is present at very low concentration levels throughout the whole process. It was confirmed that this mechanism provides a satisfactory interpretation of the experimental data in the entire accessible pH-range.

3.3. *A simple test method was developed based on initial rates in order to determine whether the hydroxo dimer reacts directly with a particular ligand or not, and this test method was used to show that the rapid formation of multinuclear iron(III) complexes only occurs with oxoanions as ligands.*

The mono- and dinuclear hydroxo complexes in aqueous solutions of iron(III) ion cannot be separated, and it is often unclear which form reacts in the process monitored spectrophotometrically at a certain wavelength in a particular system. The test method was developed to solve this problem and is based on a comparison of initial rates of absorbance change measured in two complementary kinetic experiments. If the ratio of the two initial rates is significantly different from 1.0, the observations prove that  $\text{Fe}_2(\text{-OH})_2(\text{H}_2\text{O})_8^{4+}$  reacts directly with the ligand in the substitution reaction. The test method was used with some 30 inorganic ligands, and it was found that hypophosphite, phosphite, phosphate, arsenite, arsenate, dithionate, sulfite, sulfate, selenite and periodate ions reacted directly with the hydroxo dimer.

3.4. *It was established that direct reactions between the hydroxo dimer and the ligand leads to the formations of transient dinuclear complexes with the compositions  $\text{Fe}_2(\text{OH})(\text{H}_2\text{PO}_2)(\text{H}_2\text{O})_8^{4+}$ ,  $\text{Fe}_2(\text{OH})(\text{HPO}_3)(\text{H}_2\text{O})_8^{3+}$ ,  $\text{Fe}_2(\text{OH})(\text{SO}_3)(\text{H}_2\text{O})_8^{3+}$ , and  $\text{Fe}_2(\text{OH})(\text{SeO}_3)(\text{H}_2\text{O})_8^{3+}$  in the initial phase of the reactions between iron(III) ion and hypophosphite, phosphite, sulfite, and selenite ions.*

These intermediates are formed at high iron(III) concentrations (> 1 mM) in the initial phases of the corresponding reactions. The absorbance decay at the characteristic band of the hydroxo dimer provided evidence for the formation of these complexes. The dinuclear sulfite complex was found to exhibit a weak absorption band, and the stability constant of this species could be estimated directly. The initial rate method proved that the reaction of the hydroxo dimer with the ligands is first-order with respect to both reactants in each system. The rate constants for the corresponding processes were determined considering the different protolytic reactions of the ligands. To our knowledge, similar complexes with inorganic ligands have not been reported in the literature yet.

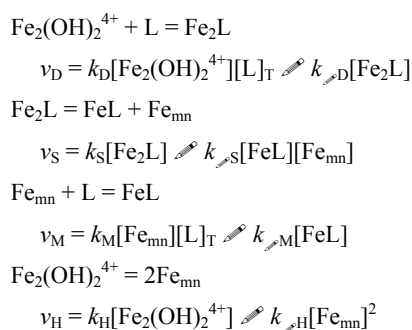
3.5. *It was verified that direct reactions between the hydroxo dimer and the ligand leads to the formations of transient tetranuclear complexes with the compositions  $\text{Fe}_4(\text{PO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$  and  $\text{Fe}_4(\text{AsO}_4)(\text{OH})_2(\text{H}_2\text{O})_{16}^{7+}$  in the initial phase of the reactions*

between iron(III) ion and phosphate or arsenate ions.

These intermediates are formed at high iron(III) concentrations ( $> 1$  mM) in the initial phases of the reactions. The absorbance decay at the characteristic band of the hydroxo dimer provided evidence for the formation of these complexes. The initial rate method proved that the reaction of the hydroxo dimer with the ligand is first-order with respect to both reactants in each reaction system. It seems to be likely that the rate determining steps in the formation of the tetranuclear complexes are the formations of the dinuclear complexes analogous to the ones mentioned in the previous paragraph,  $\text{Fe}_2(\text{OH})(\text{HPO}_4)(\text{H}_2\text{O})_8^{3+}$  and  $\text{Fe}_2(\text{OH})(\text{HAsO}_4)(\text{H}_2\text{O})_8^{3+}$ . These dinuclear intermediates are always present at very low concentration levels as they react to give the tetranuclear complexes rapidly.

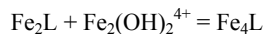
3.6. *Kinetic models were proposed to interpret the reactions between iron(III) ion and hypophosphite, phosphite, phosphate, arsenate, and selenite ions, and the rate constants for the individual reactions steps were determined.*

A common characteristic feature of these reactions is that the formation of multinuclear intermediates is followed by the formation of mononuclear complexes. The formation of these mononuclear complexes was also studied independently under conditions where the reactions of the hydroxo dimer are negligible ( $[\text{Fe(III)}] < 0,2$  mM). The following general model was postulated to interpret the measurements at iron(III) excess. The rate constants in this model are pH-dependent and the exact pH-dependences were explored:



where  $\text{Fe}_2\text{L}$  is a dinuclear iron(III) complex, whereas  $\text{FeL}$  is a mononuclear iron(III) complex. The stoichiometries of these complexes were determined in each case. For the phosphate and arsenate

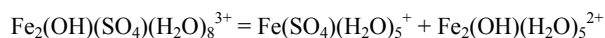
ion system a further step was included in the model as a fast pre-equilibrium:



The rate constants in the equations for  $v_M$  and  $v_H$  were determined in independent studies. The rest of the rate constants were calculated by fitting the absorbance-time traces directly to the simultaneous differential equations defined by the model. The individual pathways for each reaction were identified on the basis of the pH-dependences of the experimentally determined rate constants.

3.7. *The fast formation of the intermediate  $\text{Fe}_2(\text{OH})(\text{SO}_4)(\text{H}_2\text{O})_8^{3+}$  was verified in the initial phase of the iron(III) ion-sulfate ion reaction, and it was shown that the decomposition of this complex has a significant role during later processes.*

The formation of the intermediate was indicated by an absorbance decrease at the characteristic band of the hydroxo dimer, but the reaction was complete within the dead time of the stopped flow instrument, i.e. 1 ms, even at 5.0 °C with any initial concentrations. Thus, no kinetic information for this process could be obtained. However, the corresponding equilibrium constant could be determined on the basis of the amplitude of the absorbance changes. It was shown that the following step should be taken into account to interpret later processes during the reaction:



3.8. *Arsenite ion was confirmed to catalyze the hydrolytic reactions of iron(III) ion, and this finding was interpreted assuming the formation and decomposition of the dinuclear complex  $\text{Fe}_2(\text{OH})(\text{H}_2\text{AsO}_3)(\text{H}_2\text{O})_8^{4+}$ .*

No detectable iron(III) complexes were formed with arsenite ion in the pH-range of the present study. However, the presence of arsenite ion catalyzed the decomposition and formation of the hydroxo dimer. In order to interpret the catalytic effect, it was assumed that the complexes  $\text{Fe}(\text{H}_2\text{AsO}_3)(\text{H}_2\text{O})_5^{2+}$  and  $\text{Fe}_2(\text{OH})(\text{H}_2\text{AsO}_3)(\text{H}_2\text{O})_8^{4+}$  form at very low concentrations levels, and their reactions open a novel, arsenite-catalyzed pathway for the hydrolytic processes.

3.9. *It was proposed that the direct substitution reactions of the hydroxo dimer with inorganic ligands proceed via an  $I_d$  mechanism.*

The second-order rate constants for the substitution reactions of the hydroxo dimer with inorganic

ligands were primarily dependent on the charge of the ligand, and the neutral or uninegative protonated forms of the ligands reacted with similar rate constants. The difference between the rate constants corresponding to uninegative and neutral forms of a ligand was about an order of magnitude in each case as seen from Table 1.

**Table 1.** Rate constants for the reactions  $\text{Fe}_2(\text{OH})_2^{4+} + \text{H}_x\text{L} \rightleftharpoons \text{Fe}_2\text{L}$ ;  $T = 10.0 \text{ }^\circ\text{C}$ ;  $[\text{Fe}] = 1.0 \text{ M}$  ( $\text{NaClO}_4$ ).

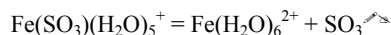
Ligand ( $\text{H}_n\text{L}$ )	$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$		
	$\text{H}_n\text{L}$	$\text{H}_{n-1}\text{L}^-$	$\text{H}_{n-2}\text{L}^{2-}$
$\text{H}_3\text{PO}_2$	$2.9 \times 10^4$	$3.5 \times 10^5$	
$\text{H}_3\text{PO}_3$	$3.3 \times 10^4$	$3.4 \times 10^5$	
$\text{H}_3\text{PO}_4$	$< 1 \times 10^4$	$1.4 \times 10^5$	
$\text{H}_3\text{AsO}_3$	$3.4 \times 10^3$ <sup>a</sup>		
$\text{H}_3\text{AsO}_4$	$8 \times 10^3$	$2.5 \times 10^5$	
$\text{H}_2\text{O}_2$	$< 5 \times 10^3$	$4.5 \times 10^4$	$2.1 \times 10^9$
$\text{H}_2\text{SO}_4$		<sup>b</sup>	$> 1.0 \times 10^7$
$\text{H}_2\text{SeO}_3$	$2.7 \times 10^4$	$4.6 \times 10^5$	

a:  $25.0 \text{ }^\circ\text{C}$ ; b: no data, any value  $< 10^6$  does not contradict the results

These results suggested that a dissociative interchange ( $\text{I}_d$ ) mechanism might be operative for these reactions. The differences between the rate constants are well interpreted by the differences of the stability of ion pairs formed between the reactants, which were calculated based on the Fuoss equation.

3.10. *A kinetic model was proposed for the reaction between iron(III) ion and sulfite ion at large iron(III) excess and it was shown that the key step of the redox process was the redox decomposition of the mononuclear sulfite complex  $Fe(SO_3)(H_2O)_5^+$  into iron(II) ion and sulfite ion radical.*

The reaction between iron(III) ion and sulfite ion was studied at large iron(III) excess, as the formation of bis- and tris-sulfite complexes could be avoided this way. It was shown that the presence or absence of oxygen, unlike at sulfite ion excess, does not influence the kinetic traces under these conditions. The key step in the redox reaction was the decomposition of the mononuclear iron(III) sulfite complex:



This reaction was the rate determining step in the overall redox process. Our method yielded an estimate for its rate constant that was considered to be more reliable than earlier values. Our experiments showed that the complex  $Fe_2(OH)(SO_3)(H_2O)_8^{3+}$  did not take part in redox reactions directly.

#### 4. Potential uses of the results

In this thesis, it was verified that the dinuclear hydroxo complex  $Fe_2(\cdot-OH)_2(H_2O)_8^{4+}$  present in aqueous iron(III) solutions could react with ligands independently of the mononuclear forms. It was established that time dependent spectral changes in a certain wavelength range primarily reflect the changes in the concentration of the hydroxo dimer. These observations are quite important for future mechanistic research on iron(III) reactions.

The test method developed for the identification of the reactions of the hydroxo dimer could be used with any (organic or inorganic) ligand. The information obtained on the general reactivity patterns of the dinuclear iron(III) center may be of significant interest for the research on the biological functions of the iron(III) ion, and may especially contribute to the understanding of the mechanisms of reactions catalyzed by enzymes containing dinuclear iron(III) moieties.

Our results in the iron(III) / sulfur(IV) system may be significant in optimizing and developing new methods for the desulfurization of plume gases, and could also provide important information for atmospheric models to clarify the role of sulfur dioxide. The results serve as

examples illustrating that reliable evaluation of kinetic curves is possible using numerical integration of kinetic models and least-squares fitting in cases where the traditional approach based on finding pseudo first-order conditions fails or yields very imprecise estimates.

## 5. Scientific publications of the author

### 5.1. Publications connected to the thesis

#### Articles

6. Gábor Lente, István Fábián

**Reactions of the Iron(III) Hydroxo Dimer with Simple Inorganic Ligands**

*Inorg. Chem.*, submitted.

5. Gábor Lente, István Fábián

**Kinetics and Mechanism of the Oxidation of Sulfur(IV) by Iron(III) at Metal Ion Excess**

*J. Chem. Soc., Dalton Trans.*, submitted, invited paper connected to the conference Dalton Discussion 4.

4. Gábor Lente, István Fábián

**A Simple Test to Confirm the Ligand Substitution Reactions of the Hydrolytic Iron(III) Dimer**

*Reaction Kinetics and Catalysis Letters*, **2001**, 73, 117-125.

3. Gábor Lente, M. Elizabeth A. Magalhães, István Fábián

**Kinetics and Mechanism of Complex Formation Reactions in the Iron(III) / Phosphate Ion System at Large Iron(III) Excess. The Formation of a Tetranuclear Complex**

*Inorganic Chemistry*, **2000**, 39, 1950-1954.

2. Gábor Lente, István Fábián

**A New Reaction Path in the Dissociation of the  $\text{Fe}_2(\text{:OH})_2(\text{H}_2\text{O})_8^{4+}$  Complex**

*Inorganic Chemistry*, **1999**, 38, 603-605.

1. Gábor Lente, István Fábián

**The Early Phase of the Iron(III) / Sulfite Ion Reaction. The Formation of a Novel Iron(III)-Sulfite Complex**

*Inorganic Chemistry*, **1998**, 37, 4204-4209.

#### Conferences

13. Gábor Lente, István Fábián (invited lecture)

**Kinetics and Mechanisms of the Oxidation of Sulfur(IV) by Iron(III) at Metal Ion Excess**

*Dalton Discussion 4*, invited speaker, January 10-13, 2002, Kloster Banz, Germany.

12. Gábor Lente, István Fábián (lecture)

**A vas(III) hidroxodimer reakciói egyszerű szervetlen anionokkal** (Reactions of the iron(III) hydroxo dimer with simple inorganic anions)

*36th Colloquium on Coordination Chemistry*, May 23-25, 2001, Pécs, Hungary.

11. Gábor Lente, István Fábán (lecture)

**Reactions of the hydrolytic iron(III) dimer  $\text{Fe}_2(\text{:OH})_2(\text{H}_2\text{O})_8^{4+}$  with simple inorganic oxoanions**

*Inorganic Reaction Mechanisms Meeting*, January 7-9, 2001, Galway, Ireland.

10. Gábor Lente, István Fábán (lecture)

**A vas(III) hidroxodimer reakciói egyszerű szervetlen ionokkal** (Reactions of the iron(III) hydroxo dimer with simple inorganic ions)

*Meeting of the Reaction Kinetics and Photochemistry Working Group of the Hungarian Academy of Sciences*, October 19-20, 2000, Gyöngyöstarján, Hungary.

9. M. Elizabeth A. Magalhães, Gábor Lente, István Fábán (poster presentation)

**Highly labile sulphito complexes of chromium(III)**

*34th International Conference on Coordination Chemistry*, July 9-14, 2000, Edinburgh, UK.

8. Zsuzsa Hadady, Gábor Lente, István Fábán (lecture)

**Vas(II)ion gyors képződésének követése szelektív kinetikai detektálással** (Monitoring of fast formation of iron(II) with selective kinetic detection)

*35th Colloquium on Coordination Chemistry*, May 26-28, 2000, Kecskemét, Hungary.

7. István Fábán, Gábor Lente, Attila Nemes, Zsuzsanna Tóth (lecture)

**Reaktív közfitermékek egyszerű szervetlen vegyületek redoxireakcióiban** (Reactive intermediates in the redox reactions of simple inorganic compounds)

*34th Colloquium on Coordination Chemistry*, May 19-21, 1999, Tata, Hungary.

6. Gábor Lente, István Fábán (poster presentation)

**Kinetic Modelling of the Reaction between Iron(III) and Sulfite Ion at Large Iron(III) Excess**

*Gordon Research Conference, Inorganic Reaction Mechanisms*, February 27- March 5, 1999, Ventura, CA, USA.

5. Gábor Lente, M. Elizabeth A. Magalhães, István Fábán (poster presentation)

**Unusual Complex Formation in the Iron(III) - Phosphate Ion System at Large Iron(III) Excess**

*Inorganic Reaction Mechanisms Meeting 98*, January 7-9, 1999, Cambridge, UK.

4. Lente Gábor, Fábán István (lecture)

**A  $\text{Fe}_2(\text{:OH})_2(\text{H}_2\text{O})_8^{4+}$  komplex bomláskinetikája** (Decomposition kinetics of the complex  $\text{Fe}_2(\text{:OH})_2(\text{H}_2\text{O})_8^{4+}$ )

*33rd Colloquium on Coordination Chemistry*, May 27-29, 1998, Paks, Hungary.

3. Gábor Lente, István Fábán (poster presentation)

**A New Reaction Path in the Formation and Decomposition of the  $\text{Fe}_2(\text{:OH})_2(\text{H}_2\text{O})_8^{4+}$  Complex**

*Inorganic Reaction Mechanisms Meeting 97*, January 9-10, 1998, Debrecen, Hungary.

2. Lente Gábor, Fábán István (lecture)

**Kompleképződés a vas(III) szulfition reakció kezdeti szakaszában** (Complex Formation in the early phase of the iron(III) sulfite ion reaction)

*32nd Colloquium on Coordination Chemistry*, June 4-6, 1997, Kecskemét, Hungary.

1. Gábor Lente, István Fábrián (lecture)

**Complex Formation and Redox Reactions in the Iron(III) Sulfite Ion System**  
*Inorganic Reaction Mechanisms Meeting 96*, December 21-23, 1996, York, UK.

## 5.2. Publications not connected to the thesis

### Articles

6. Gábor Lente, James H. Espenson

**Kinetics and Mechanism of Oxygen Transfer to Methyl(oxo)dithiolatorhenium(V) Complexes**  
*Inorganic Chemistry*, **2000**, *39*, 4809-4814.

5. Gábor Lente, Xiao-Peng Shan, Ilia A. Guzei, James H. Espenson

**Synthesis and Structure of Rhenium(IV) and Rhenium(V) Complexes with Ethanedithiol Ligands**  
*Inorganic Chemistry*, **2000**, *39*, 3572-3576.

4. Gábor Lente, Ilia A. Guzei, James H. Espenson

**Kinetics and Mechanism of the Monomerization of a Re(V) Dithiolato Dimer with Monodentate Ligands. Electronic and Steric Effects**  
*Inorganic Chemistry*, **2000**, *39*, 1311-1319.

3. Gábor Lente, Josemon Jacob, Ilia A. Guzei, James H. Espenson

**Kinetics and Crystallographic Studies of the Ligand Monomerization of a Dithiolato(methyl)-(oxo)rhenium(V) Dimer**  
*Inorganic Reaction Mechanisms*, **2000**, *2*, 169-177.

2. Josemon Jacob, Gábor Lente, Ilia A. Guzei, James H. Espenson

**Monomerization of a Rhenium(V) Dimer by Ligation**  
*Inorganic Chemistry*, **1999**, *38*, 3762-3763.

1. Gábor Lente, A. Mark Dobbing, David T. Richens

**Kinetic Studies of Water Exchange and Substitution by NCS<sup>-</sup> on the Sulfur-capped Triangular Ion [Mo<sub>3</sub>(:3-S)(:-O)<sub>3</sub>(OH<sub>2</sub>)<sub>9</sub>]<sup>4+</sup>**  
*Inorganic Reaction Mechanisms*, **1998**, *1*, 3-16.

### Invited seminars at universities

2. Gábor Lente

**Reactivity of New Methyl(oxo)rhenium(V) complexes**  
*Chemistry Seminar*, Invited Lecture, Miami University, November 18, 1999, Oxford, OH, USA.

1. Gábor Lente

**Reactivity of New Methyl(oxo)rhenium(V) complexes**

*Inorganic Chemistry Seminar*, Invited Lecture, Iowa State University, September 15, 1999, Ames, Iowa, IA, USA.

*Conferences*

4. Gábor Lente, James H. Espenson (lecture)

**A [(o-SC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>S)(CH<sub>3</sub>)Re<sup>V</sup>O]<sub>2</sub> dimer monomerizációjának mechanizmusa** (Mechanism of monomerization of the dimer [(o-SC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>S)(CH<sub>3</sub>)Re<sup>V</sup>O]<sub>2</sub>)

*35th Colloquium on Coordination Chemistry*, May 26-28, 2000, Kecskemét, Hungary.

3. Lente Gábor (lecture)

**Új metil(oxo)rénium(V) komplexek reakciói** (Reactions of novel methyl(oxo)rhenium(V) complexes)

*Meeting of the Reaction Kinetics and Photochemistry Working Group of the Hungarian Academy of Sciences*, April 27-28, 2000, Balatonalmádi, Hungary.

2. Gábor Lente, James H. Espenson (poster presentation)

**Oxygen Transfer Reactions of Novel Methyl(oxo)rhenium(V) Complexes**

*European Conference on Inorganic Mechanisms*, January 7-8, 2000, Zagreb, Croatia.

1. Gábor Lente, David T. Richens (poster)

**<sup>17</sup>O NMR Study of Water Exchange on the Mixed Oxo-Sulfido Trinuclear Incomplete Cuboidal Cluster Ion [Mo<sub>3</sub>(:3-S)(:2-O)<sub>3</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup>**

*Inorganic Reaction Mechanisms Meeting 97*, January 8-10, 1998, Debrecen, Hungary.