TO THE FACULTY COUNCIL OF THE DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BELGRADE

The faculty council of the Department of Chemistry, University of Belgrade, at meeting held on July 14, 2016, elected us as the PhD Committee to assess the compliance of the proposed PhD thesis of Milan Milovanović, master chemist, titled "Experimental and Theoretical Approaches coupled with Thermochemistry of reactions "in solutio" and the Role of noncovalent interactions" in respect to requirements and scientific justification.

Based on the reviewed documentation, we are submitting the following

REPORT

A. Basic information about the candidate

Milan Milovanović was born on September 11, 1988 in Knjaževac, Serbia, where he finished elementary and high school. He started his bachelor studies at the Department of Chemistry, University of Belgrade in 2007. He graduated in March 2012 with GPA of 8.52/10.00 and a grade of 10/10 for his diploma work. He started graduate academic studies (MSc) at the Chair of General and Inorganic Chemistry, Department of Chemistry, University of Belgrade in October 2012. He finished studies in September 2013 with GPA 10/10, and a grade 10/10 for his master’s thesis entitled "Crystallographic and theoretical study of the interactions between water molecules". He started his PhD studies at the Chair of General and Inorganic Chemistry, Department of Chemistry, University Belgrade in October 2013. In October 2014, he started PhD studies at the University of Strasbourg within the joint PhD program between University of Belgrade and University of Strasbourg. Since November 2014, he is the holder of the fellowship of the French Government for joint PhD program, and in 2015 he won the fellowship of the Fund for Young Talents - Dositeja for studies abroad.
B. Scientific Proceedings

Proceedings at international meetings (short) (category M34)

Poster presentations:


Proceedings at national meetings (short) (M64)

Oral presentation:


Poster presentation:

C. Description of PhD theme

1. Scientific Field: General and Inorganic Chemistry

2. The subject of dissertation

The subject of the proposed PhD dissertation will be the study of thermochemical parameters for a variety of organometallic systems, as well as the impact of noncovalent interactions on the studied systems. A special attention will be given to the study of London dispersion forces. The study will be based on experimental and theoretical approach. The research will take into account the reactions of organometallic systems that, in the broadest sense, can be considered as Lewis acid-base pairs. Several simple and more complex Lewis acid-base pairs will be considered: achiral, chiral, diastereomeric and frustrated.

The experimental part of the research will be based on performing the reactions of interest in isothermal titration calorimeter. In this way one can get accurate and reliable values of different parameters, such as: enthalpy of the reaction $\Delta H$, the ratio of the stoichiometric coefficients of the reaction, the reaction constant $K$. Based on these parameters, it is possible to calculate the Gibbs free energy $\Delta G$ and the entropy $\Delta S$ of reaction. Also, by performing kinetic experiments, the rate of chemical reaction, $v$, and the order of reaction, $n$, can be obtained. These experiments will also be performed in the framework of the proposed doctoral dissertation.

The theoretical part of the research will be based on quantum chemical calculations, primarily DFT-D methods. Experimentally obtained parameters will be used for testing and correcting of the existing DFT methods. In order to optimize geometries and calculate interaction energies, quantum chemical calculations will be performed on appropriate model systems of organometallic compounds. Calculated and experimentally measured values of thermochemical parameters will be compared.

3. Scientific objectives

The scientific objectives of the proposed doctoral thesis are:

1. Formation of database of thermochemical parameters for reaction systems containing various Lewis acid-base pairs (achiral, chiral, diastereomeric and frustrated) based on experimentally obtained values;
2. Finding suitable reactions for isothermal titration calorimetry experiments;
3. Testing the reaction systems that are composed of various organometallic and organic compounds, such as: reactions of tris(pentafluorophenyl)borane with different phosphines, reactions of the Fischer’s carbene series with various amines, reactions of cyclopalladated complexes with different alkynes, reactions of methyl-manganese-pentacarbonyl complex with various phosphines;
4. Synthesis, isolation and characterization of the reaction products using standard methods (elemental analysis, NMR and IR spectroscopy, mass spectrometry, single-crystal X-ray diffraction);
5. Performing suitable reactions in isothermal titration calorimeter;
6. Analysis of the results of isothermal titration calorimetry experiments and calculation of thermochemical parameters;
7. Construction of model systems for quantum chemical calculations based on crystal structures of compounds synthesized in this study or similar crystal structures found in the Cambridge Structural Database (CSD);
8. Calculations of interaction energies and thermochemical parameters of experimentally tested systems using various DFT methods;
9. Considering the role of noncovalent interactions within the tested systems, with special emphasis on the role of London dispersion forces;
10. Assesment of reliability of description of the tested and similar reaction systems using DFT methods, based on the comparison of experimental and calculated thermochemical parameters.

4. Methodology

In order to form the database of thermochemical parameters ($\Delta_H$, $\Delta_G$, $\Delta_S$) of various Lewis acid-base reaction systems (achiral, chiral, diastereomeric, frustrated), selected reactions will be carried out in isothermal titration calorimeter (Isothermal Titration Calorimetry (ITC) - TA Instruments). As a result of these experiments, the ITC thermograms of released or absorbed reaction heats will be obtained. Based on detailed analysis and mathematical modeling of the results, thermochemical parameters of interest will be computed.

Calculations of interaction energies and thermochemical parameters of investigated reaction systems will be performed using the variety of DFT-D methods, both in gas phase and in solution. Model systems will be designed based on crystal structures of synthesized systems or similar crystal structures found in the Cambridge Structural Database (CSD). Quantum chemical calculations will be performed using the software packages ADF13 and Gaussian 09. The choice of appropriate methods for all the systems will be made by comparing the obtained results with the results obtained at CCSD(T)/CBS level of theory, which is considered the gold standard of quantum chemistry.

Based on comparison of experimental and theoretical results, reliability of description of tested and similar reaction systems with used DFT methods will be assessed. Also, detailed description of the role of noncovalent interactions on the studied systems will be done.
5. Importance of the topic

In the recent years the interest among the researchers in noncovalent interactions is increasing because of their role in the structure and function of a huge number of chemical and biochemical systems. Noncovalent interactions are of particular importance in the fields of supramolecular chemistry, crystal engineering, materials chemistry and biochemistry. In addition to the importance to the fundamental science, noncovalent interactions have great practical significance. By controlling the processes that are responsible for recognition and packing, materials of desired chemical and physical properties can be obtained.

It is known that London dispersion forces are the weakest type of noncovalent interactions in terms of energy and that they are present everywhere in nature. These forces represent the important contribution to the energy of stabilization of peptide tertiary structure and other natural polymers, as well as to the spontaneous association of atomic clusters or nonpolar molecules. In addition to electrostatic interactions, London dispersion forces help in defining stereochemical outcome of many reactions; they play the important role in the process of recognition and chiral discrimination. London dispersion forces also affect the formation of the "second coordination sphere" of complex compounds.

Understanding the aspects of chemical bonding, as well as noncovalent interactions, has been enabled by the application of new theoretical methods, especially methods known as DFT-D, i.e. DFT methods corrected for dispersion. These methods provide the explanation of dispersion effects on the medium in physically meaningful ways.

The aim of this thesis is to shed a light on the role of London dispersion forces in the formation of Lewis complexes by combining experimental techniques and quantum chemical methods. The basis of this study is to determine the reference values of thermochemical parameters of reactions in solution. Experimentally obtained parameters will be added to the appropriate database of thermochemical parameters. The obtained parameters will be used for testing and parameterization of dispersion correction of DFT methods, as noted in the recent collaborative study of laboratories in which the candidate works and the research group of Prof. S. Grimme from Bonn.

6. Expected Results

In this doctoral thesis, the candidate Milan Milovanović will investigate the role of noncovalent interactions, with special emphasis on London dispersion forces, as well as thermochemical parameters of different organometallic systems in solution. The results will be published in scientific journals that are important for this scientific field. The results of the proposed doctoral thesis will give an original scientific contribution to the investigation of noncovalent interactions, in both experimental and theoretical manner. The results of experimental studies will be added to the appropriate database of thermochemical parameters. The obtained parameters will be the basis for further development of DFT-D computational methods, which will contribute to faster studying of similar reaction systems. The results will show differences in behavior of achiral, chiral, diastereomeric and frustrated Lewis acid-base reaction systems. Based on these results, it will be
possible to assess the role and contribution of noncovalent, primarily London dispersion interactions, in the stability and reactivity of the studied reaction systems.

Expected results will shed a light to some important aspects of noncovalent interactions and contribute to the development of DFT-D computational methods.
D. CONCLUSION

Based on the facts presented in this report, PhD Committee concludes that candidate Milan Milovanović, master of chemistry (MSc), meets all the requirements for working on doctoral thesis in order to obtain academic title PhD IN CHEMISTRY (DOKTOR HEMIJSKIH NAUKA).

All the elements of this report give the Committee the right to propose to the Faculty Council of the Department of Chemistry, University of Belgrade to accept the proposed Ph.D. thesis of candidate Milan Milovanović, master of chemistry (MSc), as scientifically relevant and approve working on PhD thesis titled "Experimental and Theoretical Approaches coupled with Thermochemistry of reactions "in solutio" and the Role of noncovalent interactions" in the scientific field General and Inorganic chemistry.

We suggest Dr. Snežana Zarić, Full professor at the Department of Chemistry, University of Belgrade and Dr. Jean-Pierre Djukic, Directeur de Recherches au CNRS, Université de Strasbourg, France, as supervisors of this thesis.

Members of the PhD Committee:

Prof. Dr. Snežana Zarić,
Full Professor, Department of Chemistry, University of Belgrade, supervisor

Dr. Jean-Pierre Djukic,
Directeur de Recherches au CNRS, Laboratoire de Chimie et Systémique OrganoMétalliques, Institut de Chimie, Université de Strasbourg, France, supervisor

Dr. Natalija Polović,
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Prof. Dr. Edward Brothers,
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Dr. Hani Amour,
Directeur de Recherche, HDR, Université de Pierre et Marie Curie, Paris, France

Prof. Dr. Dominique Armspach,
Professeur à l’Université de Strasbourg, France

Belgrade, September 8, 2016.