Łódź, 16/02/2021

FACULTY OF
CHEMISTRY
University of Lodz

prof. dr hab. Marcin Palusiak
Department of Physical Chemistry
Faculty of Chemistry, University of Lodz
Pomorska 163/165, 90-236 Lodz, Poland
mobile phone: +48 504984038
phone: +48 42 6355737
fax: +48 42 6355744
e-mail: marcin.palusiak@chemia.uni.lodz.pl

Thesis review: Hydrogen bond and proton transfer in self-associates and mixed complexes of phosphorus-containing acids.

Submitted by: Mulloiarova Valeriia

Saint Petersburg State University.

Reviewer: Prof. dr. hab. Marcin Palusiak

The reviewed work is dedicated to the study of the structure and properties of hydrogen-bonded complexes formed by POOH-containing acids in solution in liquefied freonic gases. The investigation was carried out by both experimental (NMR spectroscopy) and theoretical (DFT calculations) methods. The study revealed the prevalence of an unusual complexation motif: non-planar cyclic trimerization with cooperatively coupled hydrogen bonds. This finding might explain the apparent high self-association enthalpy previously reported for phosphinic and phosphoric acids. Though the presented quantum-chemical calculations do not model the polar aprotic environment used in experiments, they successfully reproduce the main

structural, dynamic and spectroscopic properties of the studied complexes, which increases the reliability of the proposed interpretation of experimental NMR spectra. The correlational dependencies between ^{31}P NMR chemical shifts and the hydrogen bond geometry might be used in the future to study various disordered systems containing POOH-acids, where direct crystallographic data on interatomic distances are not available. The hetero-complexation in a mixture of phosphinic and phosphoric acids was studied for the first time. The co-existence of cyclic hetero-dimers, hetero-trimers and even hetero-tetramers was demonstrated. In hetero-complexes not all hydrogen bonds are equivalent, which leads to occasional anticooperativity of hydrogen bonds. In total, more than 30 hydrogen-bonded species involving 6 phosphorus-containing acids were investigated, counting both homo- and hetero-associates. The proposed experimental techniques – the extremely low-temperature liquid-state NMR and the partial H/D substitution in the mobile proton sites – can be further applied to study the non-covalent interactions in other systems.

Comments:

(1) In several places of the dissertation the interaction energy is given with one or two digits after the decimal point (in kcal/mol). In other places the values are round to nearest integer. In general it should be unified across the whole dissertation. Obviously giving energy values in kcal/mol with two digits after the decimal point makes no particular sense taking into account the accuracy of the method.

(2) In section 3.3.1 Author uses ELF (Electron Localisation Function) analysis for the discussion of the resonance effect within the POOH-acids fragment. Although I agree with Authors arguments, I would point out that this method has been completely omitted in *Chapter 2. Methods and approaches*.

(3) In section 4.4.2 Author discusses cooperativity and anti-cooperativity of H-bonds in phosphinic and phosphoric acid patterns. The discussion is convincing, however, I feel the lack of explicite estimation of cooperative/anti-cooperative effect expressed by the interaction energy and its components, including additive and nonaddictive contribution to interaction energy. Although experimental results indeed seem to well support discussion in that issue, the interaction energy analysis would nicely strengthen the final conclusions, the more that Author is familiar with computational approaches while the estimation of additive and non-additive

components of interaction energy is relatively simple and does not requires any particular software or special facilities.

Te above remarks do not lower my positive assessment of the dissertation. Both experimental and computational results in general fully support discussion and final conclusions. The presentation of the material is clear and consistent. Also the editorial part of the work is in my opinion at highest level and meets all requirements. Finally, all presented conclusions are sound and substantiated. What is undoubtedly of importance in the context of PhD degree procedure, the main results of the work are presented in three publications published in high quality peer reviewed international journals, where Valeriia Mulloiarova is the first Author. Additionally, results included in the dissertation were presented by the Author at several Russian and international conferences.

In summary, I conclude that the thesis “Hydrogen bond and proton transfer in self-associates and mixed complexes of phosphorus-containing acids” presents the results of an independent scientific investigation and that Valeriia Mulloiarova meets all the criteria required to obtaining PhD degree.

E-mail: marcin.palusiak@chemia.uni.lodz.pl
Skype: Marcin Palusiak (associated with marcin.a.palusiak@gmail.com)
Phone: +48 42 6355737, mobile: +48 504984038

Łódź, 16.02.2021

(date) (signature) _____Full name / Marcin Palusiak