

REVIEW

by Prof. Dr. Nikolay Georgiev Vassilev

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of a dissertation for acquiring the educational and scientific degree "Doctor" in the field of higher education: 4. Natural Sciences, Mathematics and Informatics; Professional field 4.2. Chemical Sciences

PhD program: "Analytical chemistry"

Author: *Dimitar Genchev Stoitsov*

Topic: *NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds*

Supervisors: *Prof. DSc. Plamen Nikolov Penchev - Plovdiv University "Paisii Hilendarski" and Assoc. Prof. Dr. Marin Neykov Marinov - Agricultural University - Plovdiv*

1. General description of the materials presented

By order No. P22-1706 of 21.07.2025 of the Rector of Plovdiv University "Paisii Hilendarski" (PU), I am appointed as a member of the scientific jury for ensuring a procedure for the defense of a dissertation on the topic "NMR and vibrational spectra assignment for verification and elucidation of the structures of aromatic organic and metal-organic coordination compounds" for the acquisition of the educational and scientific degree "doctor" in a field of higher education: 4. Natural Sciences, Mathematics and Informatics; Professional field 4.2. Chemical Sciences, PhD program: "Analytical chemistry".

The author of the dissertation is Dimitar Genchev Stoitsov - a full-time doctoral student at the Department of Analytical Chemistry and Computational Chemistry with scientific supervisors Prof. Dr. Plamen Nikolov Penchev from Plovdiv University "Paisii Hilendarski" and Assoc. Prof. Dr. Marin Neykov Marinov from the Agricultural University, Plovdiv.

The set of materials presented by Dimitar Genchev Stoitsov on electronic media is in accordance with Art. 36 (1) of the Regulations for the Development of the Academic Staff of the University of Plovdiv, and includes the following documents:

- application to the Rector of the University of Plovdiv for the opening of the procedure for the defense of a dissertation;
- CV in European format;
- minutes of the departmental council, related to reporting the readiness to open the procedure and preliminary discussion of the dissertation;
- opinion from the scientific supervisors regarding the opening of a procedure for preliminary discussion of the dissertation;
- synopsis in Bulgarian and English;
- declaration of originality and authenticity of the attached documents;
- a certificate of compliance with the minimum requirements for obtaining the educational and scientific degree “doctor”;
- a list of scientific publications on the topic of the dissertation;
- copies of scientific publications;
- dissertation work;
- an appendix with all spectra of the dissertation work.

The doctoral student has attached 4 publications.

The set of materials presented by PhD student Stoitsov on electronic media is in full compliance with the requirements of the Academic Staff Development Act in the Republic of Bulgaria and the regulations for its implementation, as well as the regulations for development of the academic staff of the "Paisii Hilendarski" University.

The candidate has included a total of 4 publications in the PhD thesis, all of which have been published in specialized international journals with an impact factor or impact rank. The results of the dissertation have also been reported in a scientific forum.

2. Brief biographical data about the PhD student

Dimitar Genchev Stoitsov graduated from Plovdiv University "Paisii Hilendarski", where in 2019 he obtained a bachelor's degree in "Analysis and Control" and in 2020 a master's degree in "spectrochemical analysis". In the period from November 2021 to 2025, he is an assistant professor in the Department of Analytical Chemistry and Computational Chemistry at the Faculty of Chemistry of Plovdiv University "Paisii Hilendarski".

In the period from March 2021 to 2025, he is a full-time PhD student in the same department. The dissertation was discussed and proposed for defense at an extended meeting of the Department of Analytical Chemistry and Computational Chemistry at the Faculty of Chemistry of the University of Paisii Hilendarski, held on 26.06.2025.

3. Relevance of the topic and appropriateness of the set goals and objectives

The relevance of the dissertation is undeniable. The direct determination of the structure of a compound studied with NMR spectroscopy (from solution to structure without human intervention) is a current topic that has been worked on for a long time and was set as one of the priorities in the development of organic chemistry of this decade. The tasks set and completed in the dissertation are a step towards achieving this goal. Although we are already in the era of artificial intelligence (AI) and many algorithms are available for automatic assignment and determination of the structure of studied substances using spectral techniques (IR, Raman and NMR), knowledge and skills in this area remain indispensable in scientific practice. Improving existing databases with new reliable references to new classes of compounds, as well as correcting errors in these databases, is an integral part of scientific development.

4. Knowing the problem

The development of the general part and the literature review made a very good impression on me. The literature review systematically presents both the basics of solution NMR spectroscopy and the main techniques used, as well as the available free software for confirming and proving organic structures. The candidate demonstrates a very good knowledge of the problems he has to deal with in his scientific work. The dissertation is written on 144 pages, with the literature review covering 46 pages. The literature reference contains 157 citations, of which 153 refer to the literature review.

5. Research methodology

The candidate has formulated the goal of his dissertation work as follows: to provide fully referenced NMR data, supported by partially referenced vibrational data, for new or known organic compounds of various classes for which no or only partially and/or incorrectly referenced NMR and vibrational data exist in the literature. The tasks set are adequate for fulfilling the goal of the dissertation. The chosen methodology, including the use of both one-dimensional and two-dimensional NMR spectra, allows for the achievement of the set goal.

6. Characteristics and evaluation of the dissertation work

The PhD thesis is structured as follows: Introduction, Aim and objectives, Literature review, Methods and materials, Results, Conclusion, Contributions and Application. The Introduction

chapter proves the relevance and defines the main terms of the dissertation. The aim of the dissertation is presented and the scientific tasks of the research in the dissertation are outlined to achieve it. This is followed by a brief overview of some 1D and 2D NMR spectra, characteristic vibrational intervals and classes of organic compounds that have been studied in the dissertation. The following is a presentation of the equipment and conditions for recording vibrational spectra, NMR spectra and the atomic spectral equipment for determining the content of Au, Cu and S in the metal complexes. After a detailed and illustrated presentation of the results of the spectral relationships with figures and tables, they are summarized correctly and systematically by doctoral student Stoitsov.

7. Contributions and significance of the development for science and practice

The research contributions are both scientific and applied in nature. These contributions essentially enrich scientific knowledge with fully referenced NMR and partially referenced vibrational data for different classes of organic compounds; correction of errors in previously published and referenced NMR data for four of the organic structures included in the dissertation; enrichment of the NMRShiftDB database with the structures of fluorenylspirohydantoins and naphthopyranones and with a portion of the assigned ^1H and ^{13}C NMR data for them.

8. Assessment of dissertation publications

As mentioned above, the dissertation includes a total of 4 publications: one was published in a specialized international journal *Applied Science* with IF = 2.5 for 2024 (Q1), one in *Crystals* with IF = 2.4 for 2024 (Q2), one in *Molbank* with IF = 0.4 for 2024 (Q4) and one in *Bulgarian Chemical Communications* with SJR = 0.148 for 2024 (Q4). The results of the dissertation have also been reported at a scientific forum.

Doctoral student Stoitsov is the first author in two of the publications and the second author in the remaining two publications. It is noteworthy that in two of the publications he is also a corresponding author, which means that the doctoral student's training has been completed: from scientific work, through analysis and description of the results to the formatting and publication in scientific journals.

9. Personal participation of the PhD student

My assessment of the PhD student's personal participation in the dissertation research is based solely on the content of the dissertation and the publications on it. The way in which the introduction and the literature review of the dissertation are written shows that he is very familiar with the available literature, which has helped him to plan his scientific research clearly and precisely and to choose methodologies and approaches that allow for the realization of the goals of the dissertation work. Reading the dissertation convinces me of her in-depth knowledge of the issues being devel-

oped. The discussed arrangement of the authors and the fact that he is a corresponding author in two of the publications leaves me with no doubt about his personal involvement at every stage of the research and the publication of the results.

10. Synopsis

The synopsis is formatted according to generally accepted requirements and accurately reflects the main scientific contributions of the PhD thesis.

11. Critical remarks and recommendations

I have two critical remarks about the dissertation of PhD student Stoitsov.

The first one is related to the statement: "it is possible to encounter NOESY (even ROESY) cross signals in EXSY spectra, which can be misinterpreted as EXSY cross signals". Can the PhD student give such an example and explain the difference between NOESY and ROESY spectra?

The second is related to the putative structures of the copper and gold complexes. Is it possible to have exchange between several forms? Or structures with several metals and bridging? To me, the coordination to two far-distant oxygen atoms in Fig. 3 of the article in Applied Sciences seems unlikely.

My recommendations mainly concern the presentation of the results. Why are the correlations between experimental and predicted chemical shifts not graphically presented together with the statistical indicators of the correlation? It would be good to present experimental and simulated spectra visually. In 2-3 places in the text the term pulse is used instead of impulse.

The above notes and recommendations do not spoil the good impression of the candidate's scientific work.

12. Personal impressions

I do not know PhD student Stoitsov and my impressions of him are only from the documents submitted for the competition.

CONCLUSION

The dissertation contains scientific and applied scientific results that represent an original contribution to science and the research meets all the requirements of the Act on the Development of the Academic Staff in the Republic of Bulgaria (ADSRB), the Regulations for the Implementation of the ADSRB and the relevant Regulations of the Paisii Hilendarski University.

The dissertation shows that PhD student Dimitar Genchev Stoitsov possesses in-depth theoretical knowledge and professional skills in the scientific specialty "Analytical Chemistry and Computational Chemistry" and demonstrates qualities and skills for conducting research with original scientific contributions. Despite the presence of some minor remarks on the dissertation work and the abstract commented on above, I confidently give my positive assessment of the conducted research, the achieved results and the contributions, and I propose to the esteemed scientific jury to award the educational and scientific degree "doctor" to Dimitar Genchev Stoitsov in the field of higher education: 4. Natural Sciences, Mathematics and Informatics; Professional field 4.2. Chemical Sciences, PhD program: "Analytical chemistry".

29.09.2025

Reviewer:

(Prof. Dr. Nikolay Georgiev Vassilev)