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To the Scientific Council of the Discipline of Chemical Sciences
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Evaluation of the Doctoral Dissertation by Ms. Kateryna Kravets entitled “Host–guest complexes and assemblies based on calix[n]arenes: structural diversity and transformations”

This review has been prepared following my appointment as a reviewer in the proceedings for conferring the doctoral degree in the field of natural sciences in the discipline of chemical sciences upon Ms. Kateryna Kravets. The review is based on the doctoral dissertation entitled Host–guest complexes and assemblies based on calix[n]arenes: structural diversity and transformations, as well as the documentation provided to me. This opinion has been prepared in accordance with the criteria set forth in Article 187 of the Act of July 20, 2018—Law on Higher Education and Science.

The dissertation is written in English and is accompanied by abstracts in both English and Polish, thus fulfilling the formal requirements specified in the Act. In addition, the thesis contains a list of scientific publications, a list of conference presentations, and a list of abbreviations. The main body of the dissertation is divided into seven chapters: Introduction, Literature Review, Experimental Part, Results and Discussion, Conclusions, References, and Annex I. This structure is clear and appropriate for a doctoral dissertation in chemical sciences.

The dissertation concerns a scientifically relevant and still insufficiently explored problem, namely the structural diversity and crystallization behaviour of multicomponent macrocyclic host–guest systems. Its major strength lies in the substantial body of carefully determined and properly refined crystal structures, accompanied by detailed crystallographic analysis. The results significantly expand current structural knowledge of p-sulfonatocalix[n]arene-based host–guest complexes and represent a valuable contribution to the field of supramolecular and structural chemistry. The maturity and scientific relevance of the presented research are additionally confirmed by the publication record associated with the dissertation, which includes five scientific papers, as well as its dissemination through five oral presentations and 12 poster presentations at scientific conferences.

A minor shortcoming of the thesis is the lack of a clearly delineated research objective, which appears only within the Introduction and the Abstract. While this does not affect the scientific merit of the work, it reduces the overall clarity of the thesis structure.

The dissertation devotes substantial space to highly detailed descriptions of disorder treatment, occupancies, and refinement procedures for individual structures. Although such information is important and demonstrates significant crystallographic competence, its prominence sometimes shifts attention away from the broader chemical interpretation of the results. In my view, part of this material could have been moved to the Annex, allowing the main text to focus more clearly on the larger structural and chemical picture, especially on how guest geometry and functionality shape the crystallization landscape and direct supramolecular assembly.

The introduction to X-ray diffraction refers to the phase problem; however, it does not coherently present the fundamental objective of diffraction analysis, namely the reconstruction of the electron density. In particular, the connection between the measured intensities, the structure factor, and the electron density distribution in the crystal is not explicitly established. As a result, the description remains incomplete and does not fully reflect the physical foundations of the method.

The hydrophobic effect is introduced as a “fundamental thermodynamic principle”; however, its treatment remains largely descriptive and does not fully justify this characterization. In particular, the discussion lacks a clear explanation of the thermodynamic origin of the effect, including the role of solvent structuring and the associated entropic contributions. Furthermore, the influence of host size and shape on the hydration shell and the resulting thermodynamic response of the system is not addressed. A more rigorous physicochemical treatment would strengthen this part of the thesis.

In Chapter 4.1, in the first paragraph describing the benzimidazole derivatives and the C4S and C6S systems, the wording suggests too strong a certainty that the introduction of hydroxyl or amino substituents guarantees the formation of new synthons involving O–H... SO₃[–] or N–H... SO₃[–] interactions. While the presence of such functional groups may promote these interactions, it does not by itself ensure the formation of a specific supramolecular synthon.

These remarks, however, do not diminish my overall positive assessment of the dissertation. In my opinion, the thesis presents original and valuable scientific results and demonstrates that the candidate possesses the ability to conduct independent scientific research.

Questions for the candidate:

1. In the context of X-ray diffraction, what is the relationship between the measured intensities, the structure factor, and the electron density distribution in the crystal? How does the choice of crystallographic model influence the level of structural information that can be extracted from diffraction data?
2. The hydrophobic effect is often described as being entropy-driven. Could you comment on whether this is always the case, and how the balance between entropic and enthalpic contributions may depend on the size and nature of the solute or host–guest system?
3. The concept of the supramolecular synthon is central to crystal engineering, yet its boundaries are not always clear-cut. In your opinion, when does an intermolecular interaction become a supramolecular synthon? Which criteria would you consider essential in this context: recurrence, directionality, energetic significance, transferability between systems, or predictive value? How would you reconcile this concept with the fact that even textbook motifs, such as carboxylic acid dimers, are not necessarily the dominant arrangement in all relevant crystal structures?

In my opinion, the doctoral dissertation by Ms. Kateryna Kravets, entitled “Host–guest complexes and assemblies based on calix[n]arenes: structural diversity and transformations”, meets the requirements set forth in Article 187 of the Act of July 20, 2018—Law on Higher Education and Science. Therefore, I recommend that the dissertation be accepted and that the candidate be admitted to the further stages of the doctoral procedure.



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