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Opinion about the PhD dissertation of

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entitled

IRON AND MANGANESE COMPLEXES IN BIOMIMETIC CATALYTIC OXIDATIONS

Bashdar Ismael Meena completed his PhD studies in the Doctoral School of Chemistry and Environmental Science of the University of Pannonia, Veszprém, under the supervision of Prof. József Kaizer.

The field of the summarized research is of current international interest: high-valent non-heme iron(IV)-oxo species are active oxidants in several catalytic cycles in many biological iron dependent oxygenases, and the reactive iron(IV)-oxo intermediates are often formed in the oxygen activation processes. Nitrogen-rich polydentate ligands can stabilize high-valent metal centers, which participate in oxygen atom transfer (OAT) and hydrogen atom transfer (HAT) reactions. Oxidation reactions have a significant role in the chemical industry, too. The investigation of the biomimetic oxidation gives the opportunity of developing bioinspired reaction pathways, which can be used in the pharmaceutical industry, environmental remediation and plant protection.

The results described in the dissertation and theses are published in four papers, and the candidate is the first author in two of them. The content of the dissertation is very similar to the results published in these papers – so the work has already passed one level in the quality control test of peer review.

The literature overview is sufficiently detailed, although, somewhat descriptive in nature. Oxygen atom transfer and hydrogen atom transfer mechanisms are described in detail. After the preliminary dissertation version, three sentences about proton coupled electron transfer (PCET) were added, but these are not detailed enough, only offer a single new citation. What is more, the work done by Hammarström and co-workers is mentioned in the text but not cited properly (last paragraph on page 15).

The objectives of the research were set based on previously achieved scientific results.

The selected experimental methods (UV-vis spectrophotometry, IR, GC, GC-MS, NMR, elemental analysis) are up-to-date and suitable for reaching the objectives of the research.

The statistical methods used for data evaluation are highly inconsistent. Details of the reliability of the determined parameters are seldom given.

- The estimated errors for the rate constants and activation parameters are still missing from the dissertation. They are only given in Tables 18 and 19, and nowhere else in the main text. Actually, the tables in the Appendix show most rate constants with an estimated error but not all of them (see Table S5) and the use of the number of significant figures is still highly inconsistent.

- The first-order kinetic curves based on which Figures 11-12 and Figures 28-30 are constructed are not shown. At least one example kinetic trace should be shown in each system.
- Furthermore, a linearization method has been used to evaluate the kinetic traces (e.g. page 37). This method is badly outdated, non-linear least squares fitting must be used instead (e.g. J.H. Espenson: Chemical Kinetics and Reaction Mechanisms, McGraw-Hill, 1995, p. 17 or Curr. Opin. Chem. Eng., 2018, 21, 76-83). I think at least part of the evaluation should have been repeated with the up-to-date fitting methods.
- The evaluation of Chapter 4.9 shows a lot of turnover frequencies (TOF values). While this is not uncommon in the literature, the author should not forget the fact that this is by no means the best practice in catalysis science. Recent publications (Kozuch S, Martin JML (2012) ACS Catal 2:2787-2794. Lente G (2013) ACS Catal 3:381-382. Crooks AB et al (2015) ACS Catal 5:3342-3353. Bligaard T. et al (2016) ACS Catal 6:2590-2602.) are available to prove that the sole reliance on TOF values is usually very misleading. This should have been taken into account. Usually, using a reaction rate is much more favorable instead of a TOF. A related problem is that Figures 39 and 50 show a correlation between TOF values and potentials. TOF values clearly depend on the concentrations used in the catalytic experiment, so they are by no means characteristic of the catalyst. In such a plot, a rate constant must be used, not a TOF value. (The same comment was made in the preliminary opinion as well, but nothing has been done to improve the dissertation in this respect.)

Most of the results are compared with literature precedents whenever they are available.

I accept all the points listed in the theses as novel results to be new scientific results, although the wording of the main points does not always focus on the actual achievements (e.g. "1. Investigation of reactivities of non-heme iron catalysts in oxygen atom transfer and hydrogen atom transfer reactions, high-valent non-heme iron(IV)-oxo species were proposed as the active oxidant in catalytic and stoichiometric reactions." (This is a too general statement.) or "2. The efforts have been made ..." (This is not a result.))

The logical structure of the dissertation follows time-honored standards. However,

- pages 32 and 44 are in the 'Results and discussion' section, but these texts give literature data only!
- The total substituent effect (TE) mentioned on page 40 should have been clearly defined and references should have been given to its use.

The information content of the figures and tables are reasonably clear, although the figure captions are often not as informative as they should be.

- In Figure 11, the Figure caption says "Reaction rate", however, the axis title indicates observed rate constant (k_{obs}).
- In Figure 13, an additional text remained ("Trendvonal hiba").
- Table S10 shows an unexplained quantity called TN.
- On page 40, the phrase 'linear free energy correlation' appears. However, the classical form of this is to find a correlation between the rate constants and driving forces of a series of processes. Here this is not done: the driving force of the process is not measured, and the correlation is between the rate constant and an external parameter (such as TE or Hammett constants).

The citations in the dissertation follow one of the standards formats in Chemistry.

The dissertation looks compact and esthetic.

Although, I gave detailed comments on the preliminary form of the dissertation, which included all the critical remarks made in the present opinion, the candidate did only make very perfunctory, insufficient changes.

Despite this insufficiency, overall, I think that this theses and dissertation is suitable for organizing the public PhD defense. I recommend the dissertation for acceptance.

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