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Ústav organické chemie a biochemie
Akademie věd České republiky, v. v. i.
Institute of Organic Chemistry and Biochemistry
of the Czech Academy of Sciences

Review of the opponent

Title: Investigation of copper complexes using mass spectrometry

Candidate: Mgr. Ghazaleh Yassagi

Opponent: RNDr. PhDr. Ing. Jana Jaklová Dyrťtová, Ph.D.

General:

The Ph.D. thesis is aimed to investigation of selected copper complexes with electrospray ionization mass spectrometry, DFT calculations and IRMPD spectroscopy. The topic of the thesis is of high interest of modern physical organic chemistry. The copper catalysis as well as copper interactions are still very powerful topics to study. In the thesis, the experiments are provided in the gas phase using MS and completed by DFT calculations and data from IRMPD spectroscopy. This altogether yields to deeper knowledge of chemical structure of interacting ligands on high scientific level.

Structure and content remarks:

I appreciate the chapter "Results and discussion" is well structuralized into 3 parts. However, each part contains mostly the results and the discussion is insufficient. It is useful that after the Results is placed small (usually a half page) particular conclusion. However, I would also appreciate a conclusion in the end of the thesis as is usual. Actually there is a chapter "Conclusion", however 12 lines are not adequate to conclude the amount of results present in the thesis.

Suggestions for discussion:

- 1) Cu(I) as a free ion is the initiator of Fenton reaction. However also Cu(I) present in complex with ligand can promote the Fenton reaction. Please, discuss it with the respect to received results. Discuss also the impact of ligand to oxidation state of copper.
- 2) Theoretical results suggest that the geometries of copper and zinc complexes are different. Please, discuss it with the respect to the Zn(II), Cu(II) and Cu(I) coordination number and the evidence of discrepancies between theoretical calculations and experimental IRMPD (multiphotonic character of IRPMD experiments). (Page 42)
- 3) Cu(III) was not observed experimentally. Please, can you discuss it? (page 44-45)



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- 4) How the ionization conditions influence the oxidation state of copper? Discuss also the role of ligands.

Minor questions:

- 1) Pg. 47-50 Is it true that copper is present in the PQ complexes in Cu(I) oxidation state only?
- 2) Pg. 48 Where the water and methanol adducts during the CID experiments come from?
- 3) Fig. 3.1.11 (pg. 49) In the picture the dependences of $[\text{Na}(2)2]^+$ and $[\text{Ag}(2)2]^+$ abundances to collision energy are missing. There is only $[\text{Cu}(2)2]^+$ as a parent ion and therefore it is misunderstanding that the daughter ions $[\text{Na}(2)]^+$ and $[\text{Ag}(2)]^+$ are created from $[\text{Cu}(2)2]^+$.
- 4) Which agreement between theory and experiment is supposed as “good”?
- 5) Pg. 61 Two last lines you guess “the $[\text{Cu}(\text{L}-2\text{H})(\text{O})]^-$ undergo to rapid exothermic self-oxidation”. Please could you briefly mention the reasons, why you consider the exothermic oxidation?
- 6) Pg. 66, the first paragraph. During the CID experiments of $[\text{Cu}(\text{L}-2\text{H})(\text{CH}_3\text{COO})]^-$ you expect the competition between C-H activation and a redox process. Please could you explain and discuss it?

Conclusion:

The Ph.D. thesis has very high scientific standard, without any doubts I recommend Mgr. Ghazaleh Yassagi to admission to the defense.

In Prague, Jan 12, 2018

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RNDr. PhDr. Ing. Jana Jaklová Dyrtrtová, Ph.D.

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