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Report on the PhD Thesis of Mgr. Ševčík

The thesis mainly deals with the investigation of the kinetic behavior of Cu(II) and Ln(III) complexes with selected macrocyclic ligands bearing acetate and phosphorus acid pendant arms. The studies of Ln(III) complexes are completed with spectrophotometric measurements (absorption and emission).

Mgr. Ševčík did a considerable amount of work, which sheds light on the formation and dissociation kinetics of the studied complexes. It should be noted that this kind of studies is relatively rare in literature, since the experiments are time-consuming. Kinetic aspects of coordination compounds are often neglected during their characterization, although the obtained data are essential (i) for evaluating metallic complexes for biological applications and (ii) for rational designing new and better agents. In this context, the thesis provides useful information about the kinetic inertness of the Cu(II), Ce(III) and Eu(III) complexes with respect to the chemical structure of pendant arms. Mgr. Ševčík has thus significantly contributed to the publication of three scientific articles until now.

Formally, the submitted Thesis is well structured and the obtained data clearly presented. Concerning English, the manuscript contains few grammatical and typing errors, which are not detailed here. Many articles before nouns are missing. The sentences are sometimes too long, which makes their understanding difficult.

Remarks and comments:

Page 10-11 and Table 1: It should be noted that not all complexes with macrocyclic ligands are less toxic than open-chain ligands, e.g., DTPA. The abbreviation "Meg" is not explained.

The source (reference) for Table 1 should be given.

Page 15: The legend for Figure 3 is not sufficient - the information about the measured compounds is missing (wavelengths, solvent, reference).

Page 18: The same information appears in both paragraphs. Figure 6 is not referred in the manuscript.

Page 30: I would appreciate to see here the rate law including the species from Scheme 1.

Page 43: I would like to find typical spectral variations of Cu(II) complexes with time in this chapter (at least one example).

Page 52: The expression for k_2 does not contain α expressed by equation 19.

Page 72-73, Figures 38-40 (not referred in the text): The 3D spectra are nice, but a comparison of 2D spectra for all Eu-dotp derivatives would be probably more illustrative.

Questions:

1. The author uses sometimes " $-\log [H^+]$ " and sometimes "pH". Is there any reason to use " $-\log [H^+]$ " instead of simple "pH"?
2. Page 61-63, Figures 27-29: The emission spectra of Eu(III) are quite noisy. Why? Can you get better spectra? How big are the errors on the calculated second-order rate constants for Eu(III) in comparison with those obtained for Ce(III) from absorption spectra (there are no error bars in Figure 31, for example)?
3. Page 94: The final conclusion is quite general. Please, can you select one system (metal + ligand) you have studied in the Thesis that is the best for biological applications?

In conclusion, despite the above remarks, Mgr. Ševčík has presented a valuable piece of scientific work, which fulfills all requirements necessary for obtaining the title "PhD". He has shown creative capacities and successfully accomplished the given research project.

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