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Dear Editor,

Thank you for your email of April 29th asking for the submission of a final version of our contribution revised in the light of the reviewer's comments. Please find below a detailed response to the suggestions, comments and criticisms of the reviewer, together with a description of the modifications introduced in the revised version.

Reviewer 1

1) The thermodynamic cycle in Fig. 7 appears to ignore the possibility that the two solvated reactants may come into contact with more, or fewer, solvent molecules than the products; the participation of "bulk-innocent" solvent molecules is not balanced in the overall reaction for the condensed phase, an issue mentioned in the cited paper by Castellano and Eggers [6].

Authors reply. Figure 7 illustrates the Born-Haber cycle built using the true thermodynamic free energy changes $\Delta G_{1,1,exch}^{Lk,LaX_3}$, which have been already corrected for any changes in the chemical potential of the solvent according to eqn 10. It would be erroneous to introduce the latter correction a second time in Fig. 7.

2) The natural logarithm symbol appears to be missing in several places where the term $-RT\ln(Q)$ appears as simply $-RT(Q)$. See, for example, the y-axis labels in Figs. 3b, 4a, 5c, 6c, 12c, and the corresponding figure legends.

Authors reply. The reviewer is right and we apologize for our repetitive inadequate 'cut and paste' processes. All missing logarithm symbols have been corrected.

3) Editing Suggestions.

1. Page 1, Line 38: Change "regular solution theory" to classical solution theory.
2. Page 5, Line 39: Move the verb "may" forward to start the question "how may coordination..."
3. Page 7, Line 15: Change "product" to plural form, products.
4. Page 11, Line 7: Change "no more constant" to no longer constant.
5. Page 27, Line 42: Change "in term of" to in terms of

Authors reply. The editing suggestions have been introduced into the revised version.

Reviewer 2

1) Although the vast majority of chemical and biochemical reactions take place in liquid medium, solution chemistry tends to be overseen in many papers appearing in the literature, particularly those reporting physico-chemical or photophysical parameters. This is striking in coordination chemistry where many scientists consider that dissolution of an chelate or, worst, supramolecular assembly (host-guest chemistry), does not affect its structure. Moreover, when equilibria are indeed considered, few precautions are taken (e.g. adjusting the ionic strength, determination of activity coefficients...).

This work therefore represent a refreshing and welcome contribution to the field of solution supramolecular chemistry, drawing attention on the loopholes to be avoided. The critical view adopted by the authors and their use of the full range of solution theories (Margules equation for binary mixtures, Castellano-Egger approach, Born-Haber cycle, Onsager solvation energies) enable them to adequately understand and explain the concentration dependence of the affinities between lanthanide diketonates and tridentate ligands in non-ideal solutions.

The manuscript is well organized and well written and although displaying a relatively high level of theoretical modeling one can clearly follow the stepwise approach followed by the authors for reaching their conclusions. The experimental part is particularly well conducted, with uncertainties given for all reported experimental data and the conclusions are sound. I recommend publication.

[Authors reply.](#) We thank reviewer 2 for his/her encouraging words.

2) Abstract: in my opinion, it is difficult to determine precisely from this abstract what the authors have really done in their work. It is a nice introduction to the work, but more details should be given, following the structure of the article.

[Authors reply.](#) This paper being part of invited forum, we decided to broaden the scope of the topics and the abstract, already quite long, thus summarizes the global work done in this topics. For addressing the reviewer's suggestion, we have added two specific mentions to the precise novel work reported in this contribution.

This assumption eventually predicts an empirical linear dependence of the equilibrium reaction quotient on the concentration of the formed $[LLn(\beta\text{-diketonate})_3]$ complexes, a trend experimentally supported in this contribution for various ligands L differing in lipophilicity and nuclearity and for lanthanide containers grafted with diverse beta-diketonate co-ligands. Even if the origin of the latter linear dependence is still the subject of debate, this work demonstrates that this approach can be exploited by experimentalists for extracting reliable thermodynamic constants suitable for analyzing and comparing host-guest affinities in organic solvents.

Formatting notes from the Editorial Office

Manuscript-Please clearly label/identify the sections of the manuscript.

[Authors reply.](#) We have organized the revised ms using standard Abstract-Introduction-Results and Discussions-Conclusion as the main sections.

References- Remove "vol." from references. Volume numbers only need to be italicized

[Authors reply.](#) Done.

Supporting Information--Authors listed on the supporting information file do not match the authors listed the manuscript and Paragon Plus. Laure Guénée is listed on the SI file, but the manuscript file does not have this author listed. In addition, the SI file is missing Céline Besnard on the manuscript file -Author affiliations should be listed on the supporting information file exactly as they are on the manuscript file.

[Authors reply.](#) Done.

Thanking you in advance for your further consideration of this revised manuscript, I remain.

Yours sincerely



Claude Piguet

Professor of Chemistry