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Correction: The solution structures and relative stability constants of lanthanide–EDTA complexes predicted from computation

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Correction for 'The solution structures and relative stability constants of lanthanide–EDTA complexes predicted from computation' by Ravi D. O'Brien et al., *Phys. Chem. Chem. Phys.*, 2022, **24**, 10263–10271, <https://doi.org/10.1039/D2CP01081J>.

1. Correction to Table 1

In the published version of the manuscript, the stability constants given in Table 1 (from A.E. Martell and Robert M. Smith, "Critical Stability Constants", 1974, Plenum Press, New York) were entered incorrectly. Corrected values in Table 1 are given here in bold. The correction in Table 1 results in a larger error (38% instead of 2%) in the agreement between experiment and computation for the relative binding energy of the $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex with respect to the $[\text{La}^{3+}\text{-EDTA}^{4-}\cdot(\text{H}_2\text{O})_3]^-$ complex. Although the error is significantly larger, the trend is correct and within the same order of magnitude.

As shown by the corrected values in Table 1 here, the stability constant of the $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex was incorrectly read by the Corresponding author, from A. E. Martell and Robert M. Smith, "Critical Stability Constants", 1974. The incorrect value of 2.24 given in the original article, corresponds to the protonation $\text{p}K_{\text{a}}$ of $[\text{La}^{3+}\text{-EDTA}^{4-}\cdot(\text{H}_2\text{O})_3]^-$, not the stability constant of the $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex. The correct value of 7.84 was calculated as follows:

$$\frac{[\text{MLH}]}{[\text{M}][\text{LH}]} = \frac{[\text{MLH}]}{[\text{ML}][\text{H}]} \cdot \frac{[\text{ML}]}{[\text{M}][\text{L}]} \cdot \frac{[\text{L}][\text{H}]}{[\text{LH}]} = 10^{7.84}$$

where:

$$\frac{[\text{MLH}]}{[\text{ML}][\text{H}]} = 10^{2.24}$$

Table 1 Stability constants from experiment and calculated binding energies

Complex	Experimental stability constants ^a	Relative free energy of binding from experiment ^b	Relative binding energy from computation ^c	$\epsilon_{\text{exp-comp}}$
$[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$	7.84	0.50	0.12	38%
$[\text{La}^{3+}\text{-EDTA}^{4-}\cdot(\text{H}_2\text{O})_3]^-$	15.46	1 (reference)	1 (reference)	—
$[\text{Eu}^{3+}\text{-EDTA}^{4-}\cdot(\text{H}_2\text{O})_3]^-$	17.32	1.12	1.22	10%
$[\text{Gd}^{3+}\text{-EDTA}^{4-}\cdot(\text{H}_2\text{O})_3]^-$	17.35	1.12	1.25	13%
$[\text{Lu}^{3+}\text{-EDTA}^{4-}\cdot(\text{H}_2\text{O})_2]^-$	19.80	1.28	1.40	12%

^a $\log(K)$ values at 25 °C, from A.E. Martell and Robert M. Smith, "Critical Stability Constants", 1974, Plenum Press, New York. ^b The free energies of binding were calculated from the stability constants with **eqn (3)**. ^c The binding energy for $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ was obtained with the thermodynamic integration in **eqn (2)**, while the remaining binding energies with **eqn (1)**.



Correction

$$\frac{[\text{ML}]}{[\text{M}][\text{L}]} = 10^{15.46}$$

and¹

$$\frac{[\text{L}][\text{H}]}{[\text{LH}]} = \frac{1}{10^{9.9}}.$$

Tables S1–S3 have also been corrected in the ESI linked to the originally published manuscript.

2. Clarification regarding pH conditions of Ln-EDTA complexes

The $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex is at a protonation state that corresponds to the predominant protonation state of the unbound EDTA ligand at pH 7 (HEDTA^{3-}). The $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex is not the predominant form at pH 7 as the proton on the ligand will dissociate into the bulk solvent at pH 7. Lower pH values are required for $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ to remain the primary structure in solution.^{2,3}

Some sentences in the original manuscript correctly describe this (*e.g.*, in the Introduction: “... that of La^{3+} complexed with EDTA at a protonation state corresponding to pH ~ 7 .”); however, other sentences in the manuscript are incorrect, or unclear, (*e.g.*, in the Conclusions: “... the thermodynamic stability of the $\text{La}^{3+}\text{-HEDTA}^{3-}$ complex, corresponding to pH ~ 7 , was greatly reduced...”).

In addition, a statement in Section 3.2 (“... Ln^{3+} ions bind with EDTA much stronger at pH ~ 11 than at pH ~ 7 ...”) should be corrected to state that stronger binding of Ln^{3+} ions to EDTA occurs at pH > 7 .

Any statement in the original manuscript regarding the $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex should be interpreted so that the Ln^{3+} ion is bound to HEDTA^{3-} , which is in a protonation state that corresponds to the free ligand at pH 7, not that the $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex is the predominant state at pH 7.

The authors would like to thank Dr Robert B. Jordan (Professor Emeritus, University of Alberta) for kindly pointing out the error in the original Table 1 (and Table S1–S3), as well as the unclear language regarding the $[\text{La}^{3+}\text{-HEDTA}^{3-}\cdot(\text{H}_2\text{O})_4]^0$ complex and pH 7.

The Royal Society of Chemistry apologises for these errors and any consequent inconvenience to authors and readers.

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