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THERMODYNAMICS OF LANTHANIDES COMPLEXATION WITH TRIS(HYDROXYMETHYL)AMINOMETHANE IN AQUEOUS SOLUTION

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Complexes of lanthanide(III) (Ln^{3+}) ions are widely used in different areas including the optoelectronic devices, magnets, catalysis, sensing and imaging for biological [1] and medical purposes [2] both *in vitro* and *in vivo*. Taking into account the latter, a detailed and comprehensive study of lanthanides(III) interaction with commonly used biological buffers is strongly required. Tris(hydroxymethyl)aminomethane (Tris) is among the most often used buffer agents for biological studies. To the best of our knowledge, there is the only paper describing the complexation of Tris with one lanthanide(III) ion, namely Eu(III) [3]. The aim of this study is determining the composition, structure and stability of La(III), Ce(III), Eu(III), Gd(III) complexes with Tris. A number of modern and precise methods of analysis were used for that aim, including potentiometric titration, ^{139}La NMR, IR, MS spectroscopies, spectrofluorimetry, DSC-TG and isothermal titration calorimetry.

All the complexes formed by lanthanides(III) and Tris were found to have the stoichiometric composition of ML according to MS and TG-DSC data. Complex and free ligand have different thermal destruction patterns, which confirms the complex formation. IR spectra shows that hydroxyl groups are probably involved into complexation. Stability constants of La(III), Ce(III), Eu(III), Gd(III) complexes with Tris determined by different methods are given (Table 1).

Table 1. Stability constants of La(III), Ce(III), Eu(III), Gd(III) complexes with Tris.

Method	lg $\beta_{La(III)\text{-}Tris}$	lg $\beta_{Ce(III)\text{-}Tris}$	lg $\beta_{Eu(III)\text{-}Tris}$	lg $\beta_{Gd(III)\text{-}Tris}$
Potentiometry	2.53±0.09	2.25±0.11	2.42±0.09	2.41±0.15
Spectrofluorimetry	-	-	2.39±0.12	2.81±0.46
^{139}La NMR	2.67±0.33	-	-	-

The inaccuracies in Table 1 are the half-widths of confident interval at confident probability of 0.95 and sample size of 3 to 4 experiments.

The stability constants of different ions complexes are close to each other. It is worth noting that the protonation constant of Tris calculated from our experimental data (lg β_{HTris} = 8.09±0.03) is close to the recommended literature value lg β_{HTris} = 8.076 [4]. The lg $\beta_{Eu(III)\text{-}Tris}$ value is also in good agreement with the results of [3] (lg $\beta_{Eu(III)\text{-}Tris}$ = 2.3; 2.44). Isothermal titration calorimetry was used for determining the changes in enthalpy of lanthanides(III) complexation reaction with Tris.

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