

Abstract

The binding energies between TREN-CMPO-OEt and the lanthanides *in vacuo* and in a water solvated environment were calculated using PM6. The gas phase calculations indicated a decreasing trend in binding energies along the series while the water solvated calculations better represented the experimentally known selectivity of the chelator to terbium.

Background

Lanthanides are important resources for a wide range of applications due to their unique chemical properties. They are commonly harvested from ore deposits, but a growing alternative source is through the liquid-liquid partitioning of lanthanide byproducts in nuclear waste using lanthanide selective chelators. Consequently, there is an abundance of experimental work on the design and synthesis of these types of chelators. A present problem with this area of research is the poor theoretical framework for lanthanide selectivity. The research presented attempts to fill in this gap using exhaustive quantum chemical computation. This is accomplished by investigating the binding energetics between the lanthanides and the tris-2(-aminoethylamine) carbamoylmethyl phosphine oxide ethoxy (TREN-CMPO-OEt) chelator synthesized by Sartain et al.¹ and by comparing our results with the known extraction percentages reported by Patterson et al.²

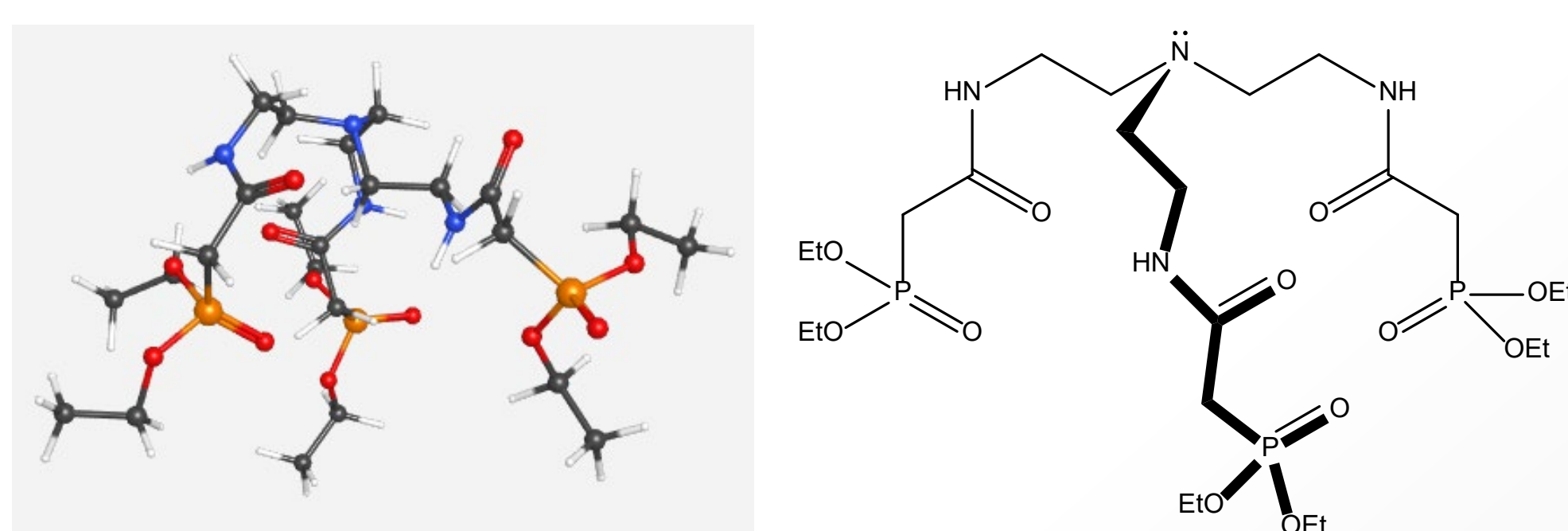


Fig 1. Tris-2(-aminoethylamine) carbamoylmethyl phosphine oxide ethoxy.

Lanthanide	Extraction %	Lanthanide	Extraction %
La	5 ± 1	Tb	18 ± 5
Ce	4 ± 1	Dy	4.9 ± 0.7
Pr	3 ± 1	Ho	9 ± 2
Nd	3.5 ± 0.8	Er	5.5 ± 0.8
Sm	1.2 ± 0.4	Tm	7 ± 1
Eu	8 ± 1	Yb	6 ± 1
Gd	1.4 ± 0.1	Lu	2 ± 1

Fig 2. Lanthanide extraction percentages of TREN-CMPO-OEt.

Methodology

The geometry optimizations and potential energy surface calculations of the systems were performed using MOPAC's PM6³ (Hartree-Fock) with the keyword Sparkle⁴ for lanthanide-specific computations. The temperature for each system was set to 293.15 K (20 °C). The lanthanide and chelator coordination ratio was 1:1. One set of calculations was *in vacuo* while another set of calculations was in a water solvated environment. For the water solvated systems, three water and nitrate molecules were included within the first solvation shell while forty water molecules were included in the outer solvation shell of the complex in order to model their aqueous phase⁵. All computations were performed through the COMET cluster via XSEDE.

Geometry Optimizations

Due to the lack of experimental data for the starting geometry of the lanthanide complexes, we relied on the built-in geometry optimizer of MOPAC to approximate their low energy configurations. The molecules are visualized through WebMO⁶.

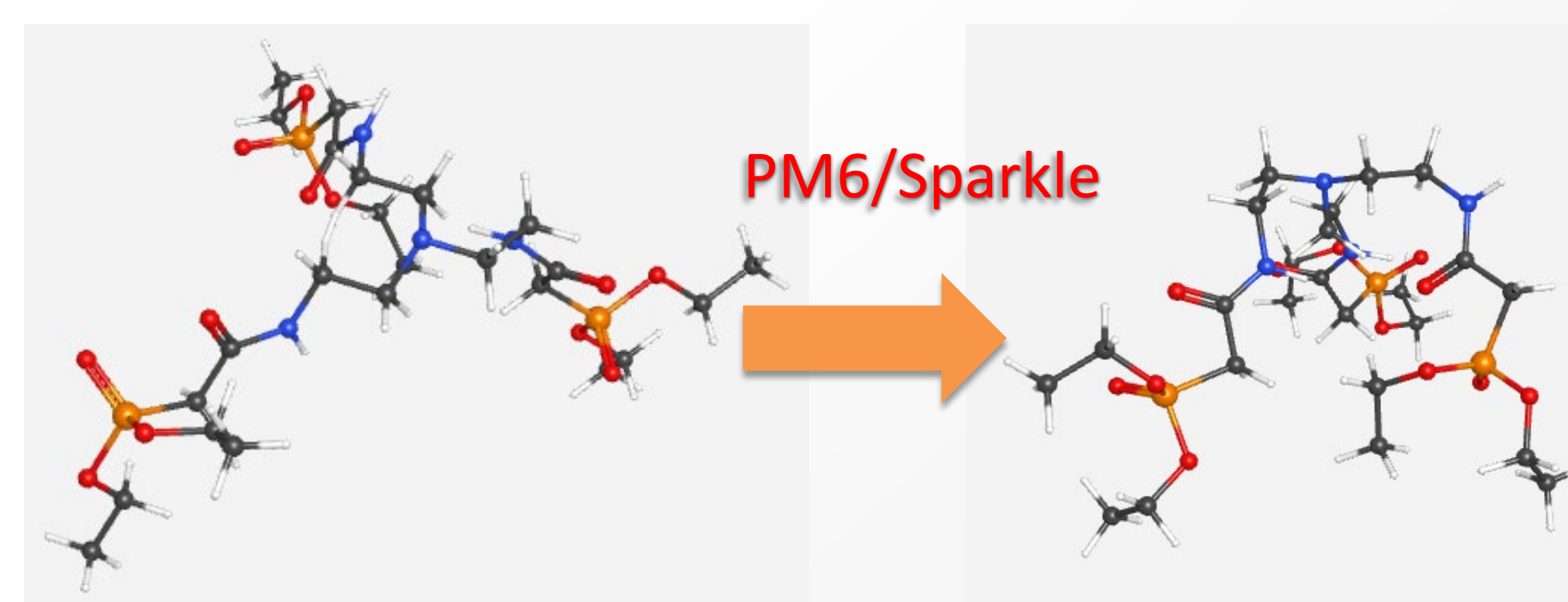


Fig 3. Geometry optimization of TREN-CMPO-OEt using PM6 with keyword Sparkle.

Binding Energies

The binding energies of each system are determined from the potential energy surfaces between the lanthanide complex, the chelator, and the lanthanide ion using the given formula:

$$E_{bind} = E_{complex} - E_{chelator} - E_{ion} \quad (1)$$

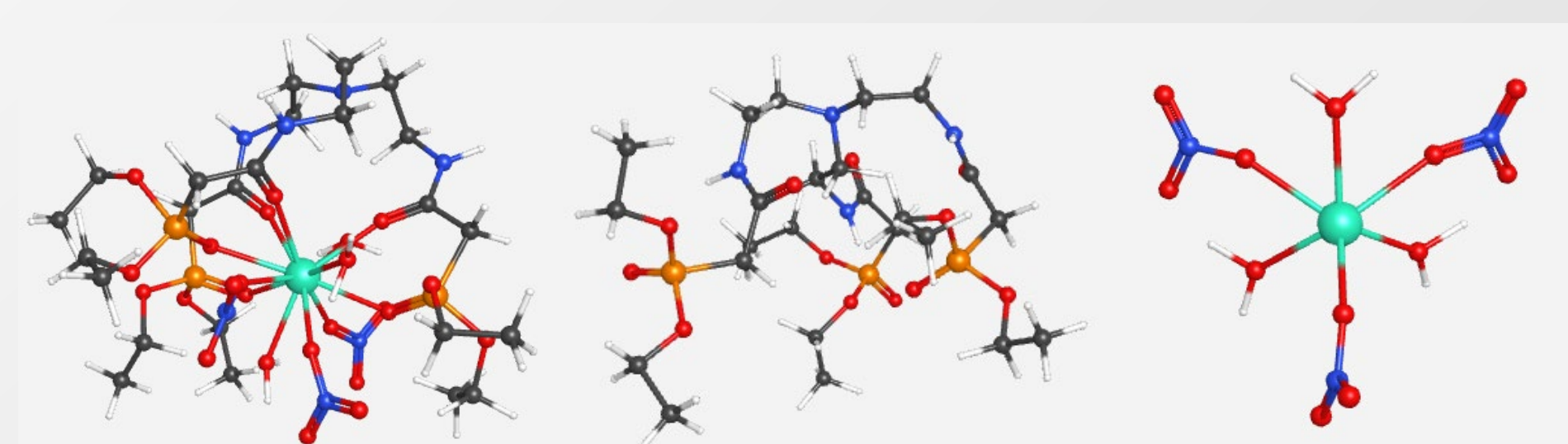


Fig 4. (Left) Lanthanide complex, (middle) chelator, (right) lanthanide ion.

Results & Discussion

The binding energy trends observed from the potential energy surface calculations of each system behave in significantly different manners. In the gas phase, the trend suggests a decreasing stability in binding energies along the lanthanide series, which may correspond with increasing atomic size. On the other hand, the trend in the solvated phase seems more erratic but is a markedly better representation of the extraction percentages obtained by Patterson et al.

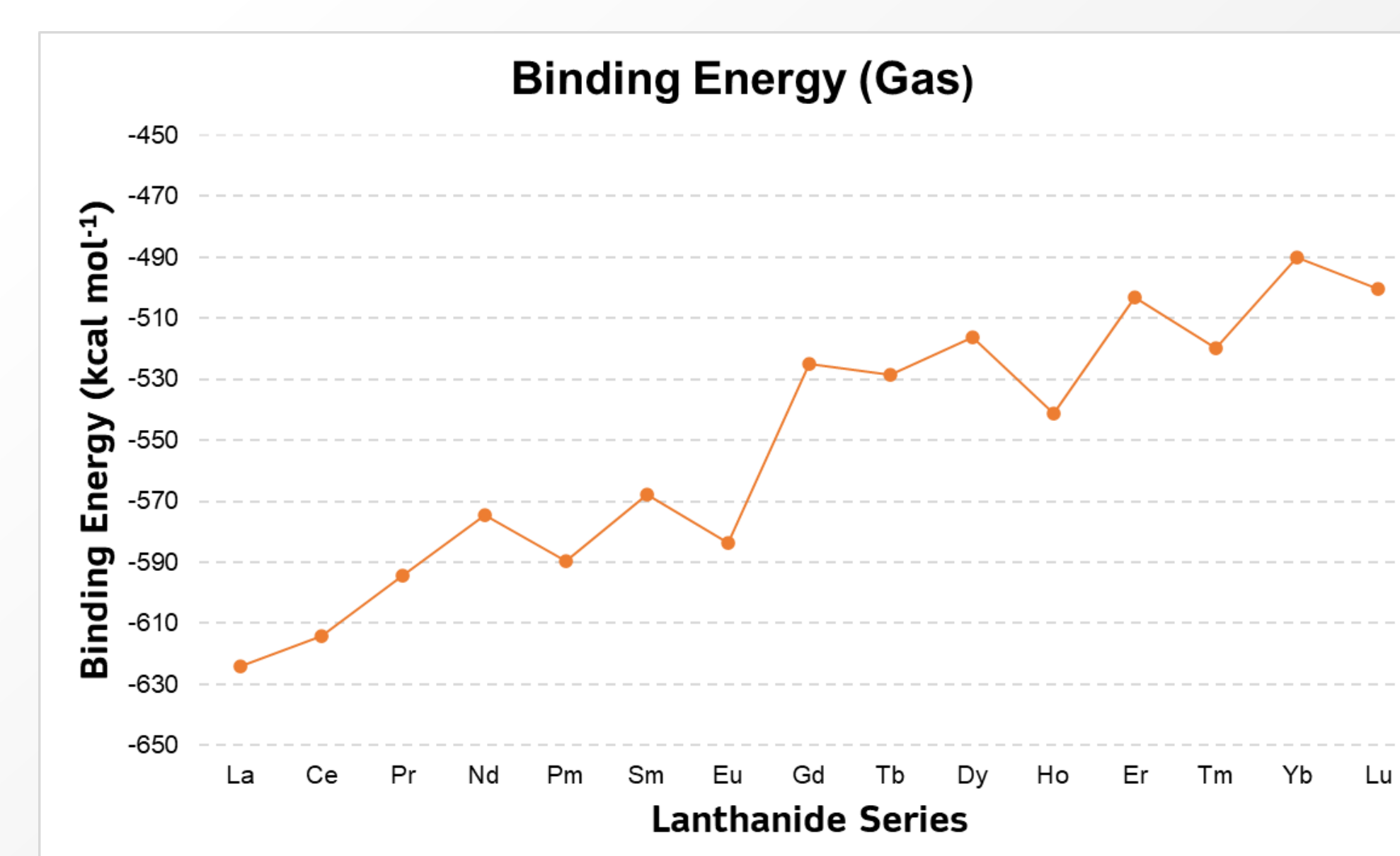


Fig 5. Binding energy trend (in kcal/mol) for the gas phase lanthanide complex systems.

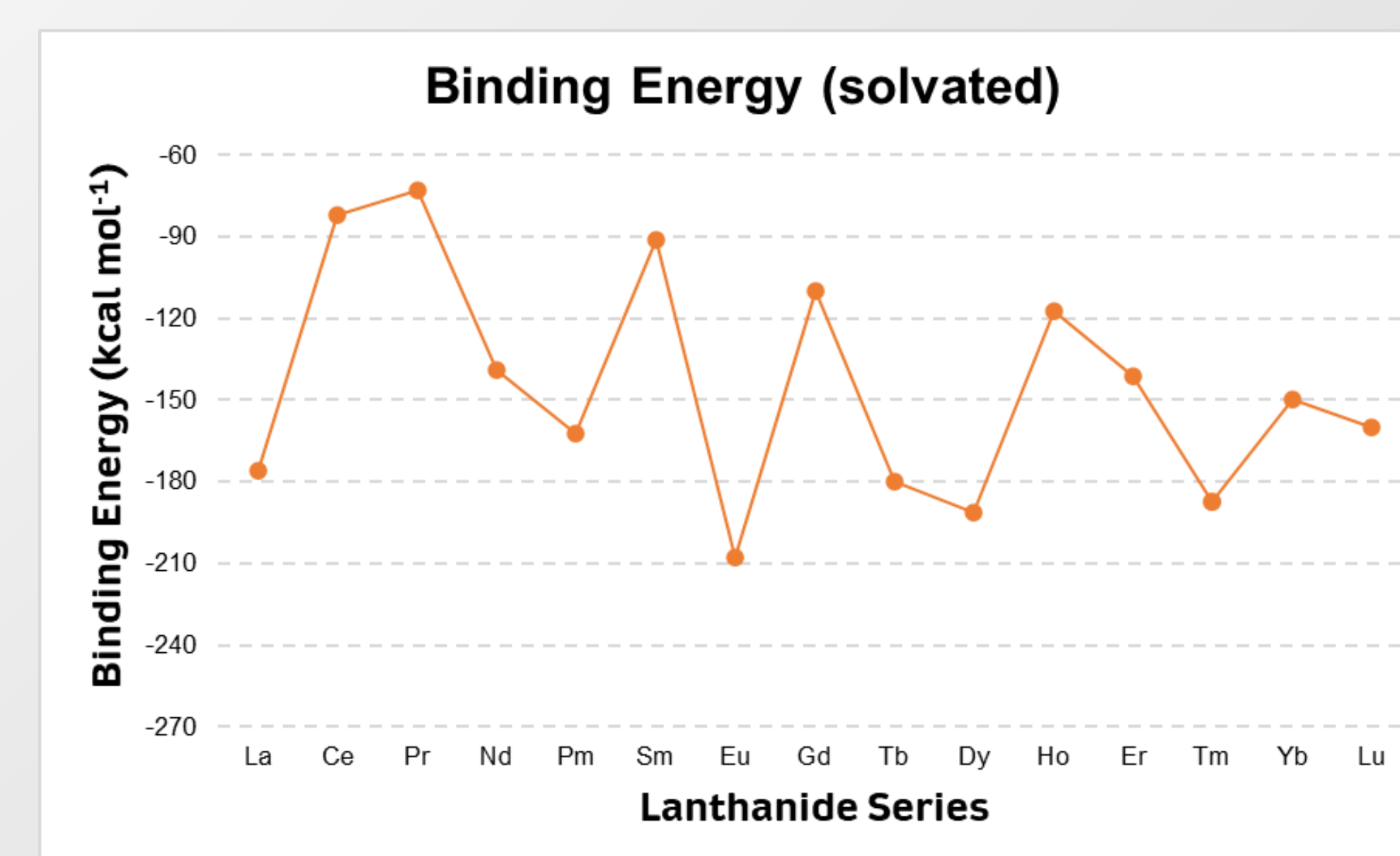


Fig 6. Binding energy trend (in kcal/mol) for the water solvated lanthanide complex systems.

The results seem to indicate that solvents may participate in some form of intermolecular bonding that facilitates better binding energies between the lanthanides and the chelator. Further investigations in explicit solvation with different solvents through molecular dynamics are ongoing.

Future Work

Following these results, we are currently investigating the effects of solvation for the lanthanide complexes through molecular dynamics using xtb's GFN-FF⁷. Other factors such as the effect of temperature in the system as well as different lanthanide-chelator binding ratios will also be explored. We also plan to utilize vibrational frequency analysis in order to locate the global minimum energy of the lanthanide complexes. The factors contributing to the most stable configurations will be expressed in the DFT level calculations in order to best approximate the binding energies of the lanthanide complexes using Gibbs free energy as a representation due to its enthalpic and entropic contributions.

Acknowledgements

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