# Supporting Information

## Identifying Coordination Geometries of Metal Aquaions in Water: Application to the case of Lanthanoid and Actinoid Hydrates

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**Intermolecular ion-water potential**

The monoatomic cation, M(III), (M being La, Lu, Ac or Cf) is described by a positive charge, $Z_{\mathrm{M}} = 4$, and a mobile negative charge density, $\rho_{\mathrm{M}}$ with a total charge, $q_{\mathrm{M}} = -1$, joined to the nucleus by a spring of force constant, $k_{\mathrm{M}}$(see Figure S1). The intra-atomic energy is defined by:

$$U_{intra} = \frac{1}{2} k_{\mathrm{M}} \cdot r^2 \tag{1}$$

where $r$ is the distance between the nucleus and its associated mobile charge density. In the absence of an external field, the equilibrium position of the oscillator is located on the nucleus and $U_{intra} = 0$.

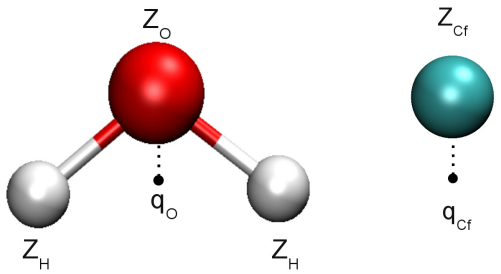


Figure S1: Schematic representation of MCDHO model for the water molecule and the metal cation.

The incorporation of the MCDHO model to the new potential needs the consideration of the following intermolecular terms for the M(III)-$H_2O$ interaction:

- Classical interaction between the mobile charge densities, $q_{\mathrm{O}}$ and $q_{\mathrm{M}}$, given by a two-exponential function:

$$U_{inter}(q_{\mathrm{O}}, q_{\mathrm{M}}) = A_{\mathrm{MO}} \cdot e^{-\alpha_{\mathrm{MO}} \cdot r_{\mathrm{MO}}} + B_{\mathrm{MO}} \cdot e^{-\beta_{\mathrm{MO}} \cdot r_{\mathrm{MO}}} \tag{2}$$

  where $r_{\mathrm{MO}}$ is the distance between the mobile charge densities. $A_{\mathrm{MO}}$, $\alpha_{\mathrm{MO}}$, $B_{\mathrm{MO}}$ and $\beta_{\mathrm{MO}}$ are fitting parameters.

- Classical interaction between the M nucleus, $Z_{\mathrm{M}}$, and those of the water molecule, $Z_i (i \equiv$O, H), is given by a two-exponential function as well:

$$U_{inter}(Z_i, Z_{\mathrm{M}}) = C_{\mathrm{M}i} \cdot e^{-\gamma_{\mathrm{M}i} \cdot R_i} + D_{\mathrm{M}i} \cdot e^{-\delta_{\mathrm{M}i} \cdot R_i} \tag{3}$$

  where $R_i$ is the distance between the M nucleus and each $i$-th nucleus of the water molecule, and $C_{\mathrm{M}i}$, $\gamma_{\mathrm{M}i}$, $D_{\mathrm{M}i}$ and $\delta_{\mathrm{M}i}$ are fitting parameters.

- Electrostatic interaction between the water mobile charge density, $q_{\mathrm{O}}$ and the M nucleus, $Z_{\mathrm{M}}$:

$$U_{inter}(q_{\mathrm{O}}, Z_{\mathrm{M}}) = \frac{q_{\mathrm{O}} Z_{\mathrm{M}}}{r^{'}} \left[1 - \left(\frac{r^{'}}{\lambda^{'}} + 1\right) e^{-2r^{'}/\lambda^{'}}\right] \tag{4}$$

  where $r^{'}$ is the distance between the center of $\rho_{\mathrm{O}}$ and the M nucleus and $\lambda^{'}$ is the intermolecular screening described in the original MCDHO model[**?**].

- Electrostatic interaction between the M mobile charge density, $q_{\mathrm{M}}$, and each of the charges on the water molecule nuclei, $Z_i (i \equiv$O, H):

$$U_{inter}(Z_i, q_{\mathrm{M}}) = \frac{Z_i \mathrm{q}_{\mathrm{M}}}{r_i} \left[1 - \left(\frac{r_i}{\lambda^{'}_{\mathrm{M}}} + 1\right) e^{-2r_i/\lambda^{'}_{\mathrm{M}}}\right] \tag{5}$$

  where $r_i$ is the distance from the $\rho_{\mathrm{M}}$ center to $Z_i$ and $\lambda^{'}_{\mathrm{M}}$ is the corresponding intermolecular screening.

Thus, the interaction energy for a cluster with $N$ water molecules is computed by the expression:

$$\begin{aligned} U = \sum_{S=1}^{N} \Bigg( \sum_{i \in S} \sum_{j \in T} [U_{inter}(Z_i, Z_j) + U_{inter}(q_i, q_j) \\ + U_{inter}(q_i, Z_j) + U_{inter}(q_j, Z_i)] + \sum_{i \in S} \frac{1}{2} k_i \cdot r_{ii}^2 + \frac{1}{2} k_M \cdot r^2 \Bigg) \end{aligned} \tag{6}$$

where $S$ runs over the water molecules and $T$ over the M.

Table S1: Fitted parameters of the potentials (in a.u.).

| | **La** | **Lu** | **Ac** | **Cf** |
|---|---|---|---|---|
| $k_{\mathrm{M}}$ | 1.01107 | 1.12522 | 1.712844 | 0.960727 |
| $\lambda^{'}_{\mathrm{M}}$ | 0.75010 | 0.54790 | 0.292704 | 0.635312 |
| $A_{\mathrm{MO}}$ | 60.04400 | 253.49280 | 328.983209 | 568.073911 |
| $\alpha_{\mathrm{MO}}$ | 1.32059 | 1.78930 | 1.951373 | 2.214706 |
| $B_{\mathrm{MO}}$ | -10.36074 | -56.92027 | 0.182997 | -0.138243 |
| $\beta_{\mathrm{MO}}$ | 0.99410 | 1.20578 | 0.402498 | 0.475451 |
| $C_{\mathrm{MH}}$ | 41.50598 | 103.56302 | 12.181625 | 11.141950 |
| $\gamma_{\mathrm{MH}}$ | 2.65323 | 3.79588 | 0.565244 | 0.933736 |
| $D_{\mathrm{MH}}$ | 0.00214 | 0.00132 | -11.812755 | -13.336449 |
| $\delta_{\mathrm{MH}}$ | 1.83328 | 2.29914 | 0.555489 | 0.999286 |

## Details of MD simulations

- 1 cation + 1000 water molecules.
- Cubix box with length chosen to get experimental water density= 0.997 g $cm^{-3}$ at simulation conditions.
- NVT ensemble with T=300K
- PBC and Ewald sum.
- MD simulations have been carried out using the Dynamical shell model (P.J.Mitchell and D. Fincham, *J. Phys. Condens. Matter* **1993**, 5, 1031-1038) to account for the polarizable MCDHO model.
- A modified version of the DL-POLY Classic code (W. Smith, T.R. Forester and I.T. Todorov, DL-POLY v. 2.19; STFC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, Cheshire, UK 2012).
- 1ns production time.

## Potential Energy Surface Building

The interaction energies to be fitted are obtained from ab initio calculations obtained at the level indicated in the following table.

Table S2: Quantum mechanical methods[a]

| M(III) | DFT | Pseudopotential[b] |
|---|---|---|
| **La** | M06 | ECP46MBW |
| **Lu** | M06 | ECP60MBW |
| **Ac** | BP86 | ECP78MBW |
| **Cf** | BP86 | ECP87MBW |

(*a*) Basis sets from:
M. Dolg et al. Theor.Chem.Acc. **1989**, *75*, 173-194; **1993**, *85*, 441-450
J. Yang et al. Theor.Chem.Acc. **2005**, *113*, 212-224.
(*b*) Pseudopotentials taken from http://www.theochem.uni-stuggart.de

It is worth pointing out that the quasi-relativistic effective core potential (RECP) were specifically developed by Dolg and col.[6] for the lanthanides and actinides trivalent cations. Their recommended basis sets for the valence orbitals were used and aug-cc-pvdz basis sets for the O and H atoms.

Table S3: M–O Distances (Å) and hydration numbers corresponding to the first and second hydration shells, and hydration energies.

| **Cation** | $R_{\mathbf{M\text{-}O_I}}$ | | | $N_{\mathbf{I}}$ | | | $R_{\mathbf{M\text{-}O_{II}}}$ | | | $N_{\mathbf{II}}$ | | | $\Delta H_hydr$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | This work | Theor. | Exptal. | This work | Theor. | Exptal. | This work | Theor. | Exptal. | This work | Theor. | Exptal. | This work | Theor. | Exptal. |
| La | 2.62 | 2.65[3]<br>2.56[4]<br>2.52[7] | 2.58[1]<br>2.55-2.64[2]<br>2.54[5]<br>2.52-2.65[6]<br>2.60[8] | 9.1 | 9.5[3]<br>8.9[4]<br>9.0[7] | 9.1[1,8]<br>9[2]<br>9.2[5]<br>9[6] | 4.72 | 5.0[3]<br>4.68[4]<br>4.65[7] | 4.63[6] | 20 | 23[3]<br>15[4]<br>19[7] | 18[6] | -745 ±60<br>-811[10] | -792[9] | -792[11] |
| Lu | 2.37 | 2.32[7] | 2.35[8]<br>2.37[1]<br>2.31[15] | 8 | 8[7] | 8[8]<br>8[1]<br>7.7[15] | 4.59 | 4.50[7] | | 18 | 18[7] | | -838 ±60 | -896[9]<br>-897[10] | -883[11] |
| Ac | 2.65 | | | 8.7 | | | 4.69 | | | 22 | | | | | |
| Cf | 2.47 | 2.37-2.49[13] | 2.42-2.55[12]<br>2.42[14] | 7.8 | | 9[12,16]<br>8.5[14] | 4.69 | | | 19 | | | | | |

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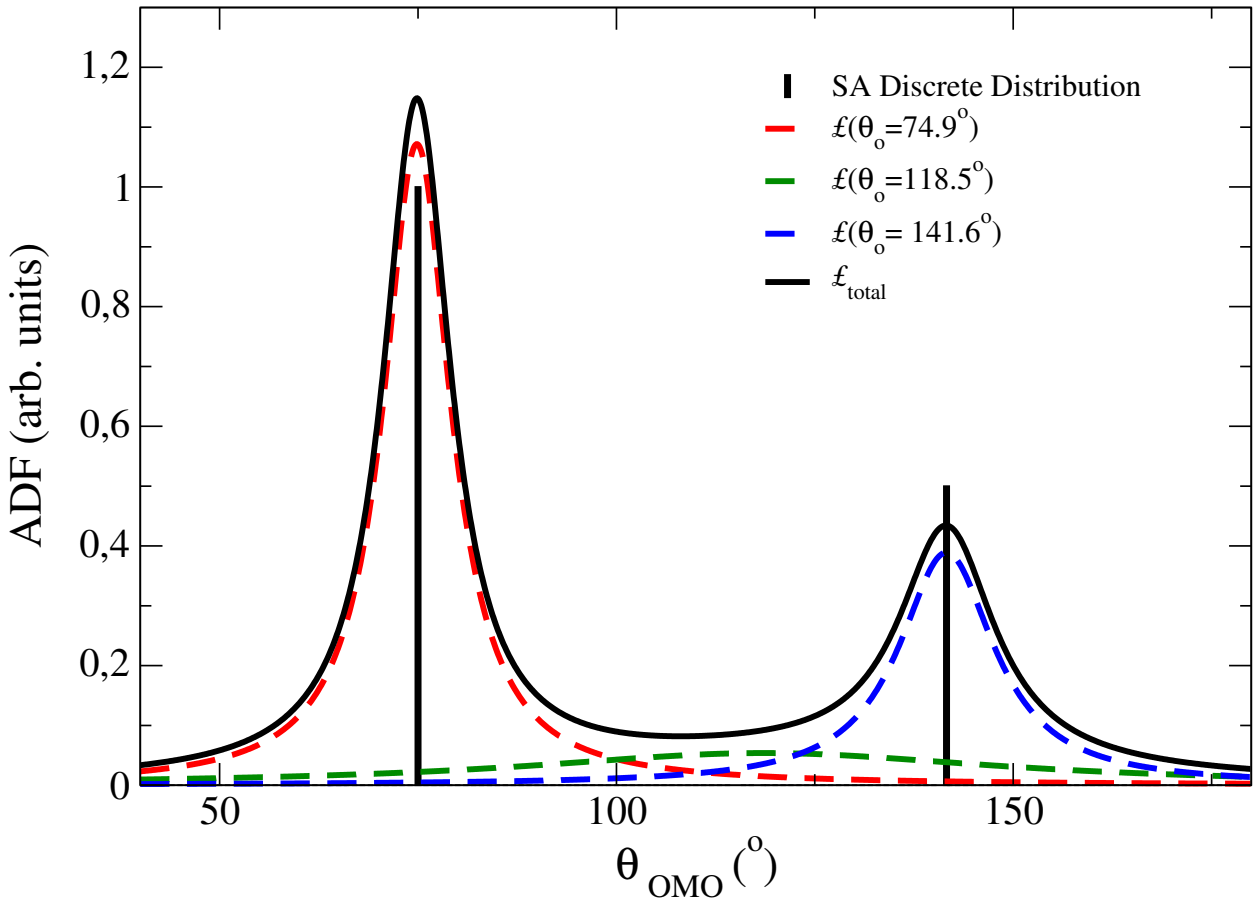


Figure S2: Linear combination of Lorentzian functions centered on the OMO angles of a SA polyhedron.

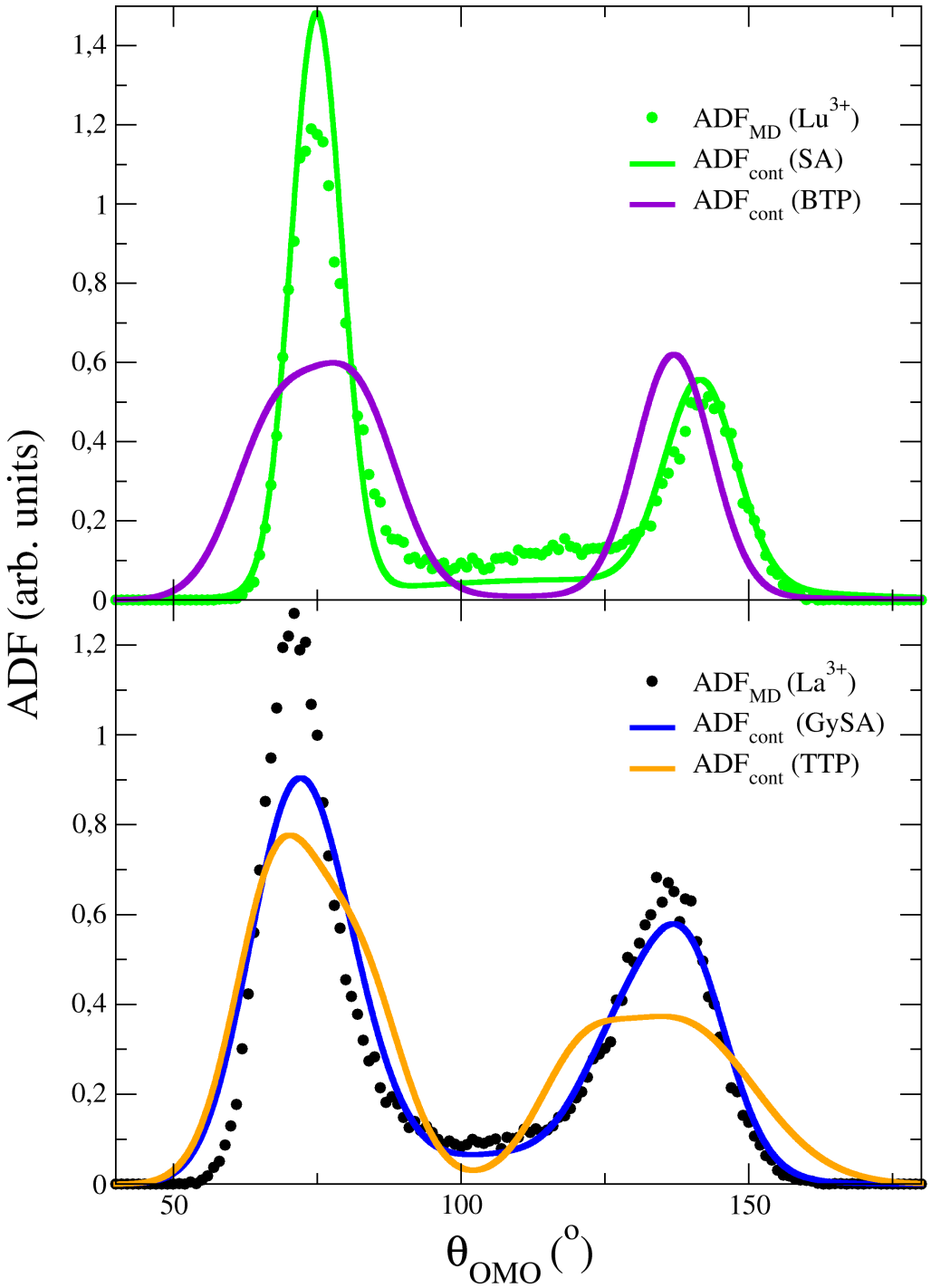


Figure S3: Top: Comparison of the simulation ADFs for $Lu^{3+}$(green dots) and the $ADF_{cont}$ built from Gaussians for the SA (green line) and BTP (magenta line) 8-coordination polyhedra Bottom: Comparison of the simulation ADFs for $La^{3+}$ (black dots) and the $ADF_{cont}$s built from Gaussians for the GySA (blue line) and TTP (orange line) 9-coordination polyhedra

Table S4: Parameters to build the Lorentzian functions associated to the different angles of the polyhedron representative of the octa-fold and ennea-fold coordination.

Data from reference polyhedra

| **SA** | | **Cube** | | **TTP** | | **GySA** | |
|---|---|---|---|---|---|---|---|
| $\theta_o^{ref}$ | *Degeneration* | $\theta_o^{ref}$ | *Degeneration* | $\theta_o^{ref}$ | *Degeneration* | $\theta_o^{ref}$ | *Degeneration* |
| 74.86 | 16 | 70.53 | 12 | 67.79 | 12 | 66.8 | 4 |
| 118.53 | 4 | 109.47 | 12 | 81.79 | 9 | 68.5 | 4 |
| 141.59 | 8 | 180.0 | 8 | 120.00 | 3 | 73.8 | 8 |
| | | | | 135.59 | 6 | 81,1 | 4 |
| | | | | 139.11 | 6 | 105.4 | 2 |
| | | | | | | 127.3 | 4 |
| | | | | | | 133.7 | 2 |
| | | | | | | 139.1 | 8 |

Data taken from QM calculations and MD simulations used to derive Eq. (3)

| **Cf(SA)** | | | | **Lu(SA)** | | | |
|---|---|---|---|---|---|---|---|
| $\theta_o^{QM}$ | $\overline{k}$ | $\theta_o^{ADF}$ | $\Delta\theta_{FWHH}$ | $\theta_o^{QM}$ | $\overline{k}$ | $\theta_o^{ADF}$ | $\Delta\theta_{FWHH}$ |
| 77.3 | 0.0356 | 74.0 | 12.5 | 77.6 | 0.0592 | 74.0 | 11.7 |
| 115.4 | 0.0070 | — | — | 115.1 | 0.0084 | — | — |
| 142.3 | 0.0414 | 143.0 | 16.2 | 142.3 | 0.0419 | 143.0 | 15.4 |

| **La/Ac(TTP)** | | | |
|---|---|---|---|
| $\theta_o^{QM}$ | $\overline{k}$ | $\theta_o^{ADF}$ | $\Delta\theta_{FWHH}$ |
| 69.7 | 0.0363 | 70.6 | 15.3 |
| 80.0 | 0.0344 | | 16.1 |
| 120.0 | 0.0367 | — | 15.1 |
| 134.1 | 0.0191 | 136.2 | 29.0 |
| 139.3 | 0.0207 | | 26.8 |

Lorentzian parameters employed to construct Figs. 3 and 4 using Eqs. 1 and 3.

| | **SA** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cf** | | | **Lu** | | | | |
| $\theta_0$ | 74.86 | 118.53 | 141.59 | 74.86 | 118.53 | 141.59 | | |
| $A$ | 16 | 4 | 8 | 16 | 4 | 8 | | |
| $\Gamma$ | 17.2 | 87.6 | 14.8 | 10.4 | 73.0 | 14.6 | | |
| | **BTP** | | | | | **Cube** | | |
| | **Cf** | | | | | **Cf** | | |
| $\theta_0$ | 67.79 | 81.79 | 120. | 135.59 | 139.11 | 70.53 | 109.47 | 180.0 |
| $A$ | 8 | 9 | 1 | 6 | 4 | 12 | 12 | 4 |
| $\Gamma$ | 17.2 | 17.2 | 87.6 | 14.8 | 14.8 | 17.2 | 87.6 | 14.8 |
| | **TTP** | | | | | | | |
| | **La/Ac** | | | | | | | |
| $\theta_0$ | 67.79 | 81.79 | 120.00 | 135.59 | 139.11 | | | |
| $A$ | 12 | 9 | 3 | 6 | 6 | | | |
| $\Gamma$ | 16.7 | 16.9 | 17.8 | 32.1 | 29.6 | | | |
| | **GySA** | | | | | | | |
| | **La/Ac** | | | | | | | |
| $\theta_0$ | 66.8 | 68.5 | 73.8 | 81.1 | 105.4 | 127.3 | 133.7 | 139.1 |
| $A$ | 4 | 4 | 8 | 4 | 2 | 4 | 2 | 8 |
| $\Gamma$ | 16.9 | 16.9 | 16.9 | 17.9 | 32.1 | 16.7 | 32.1 | 16.7 |

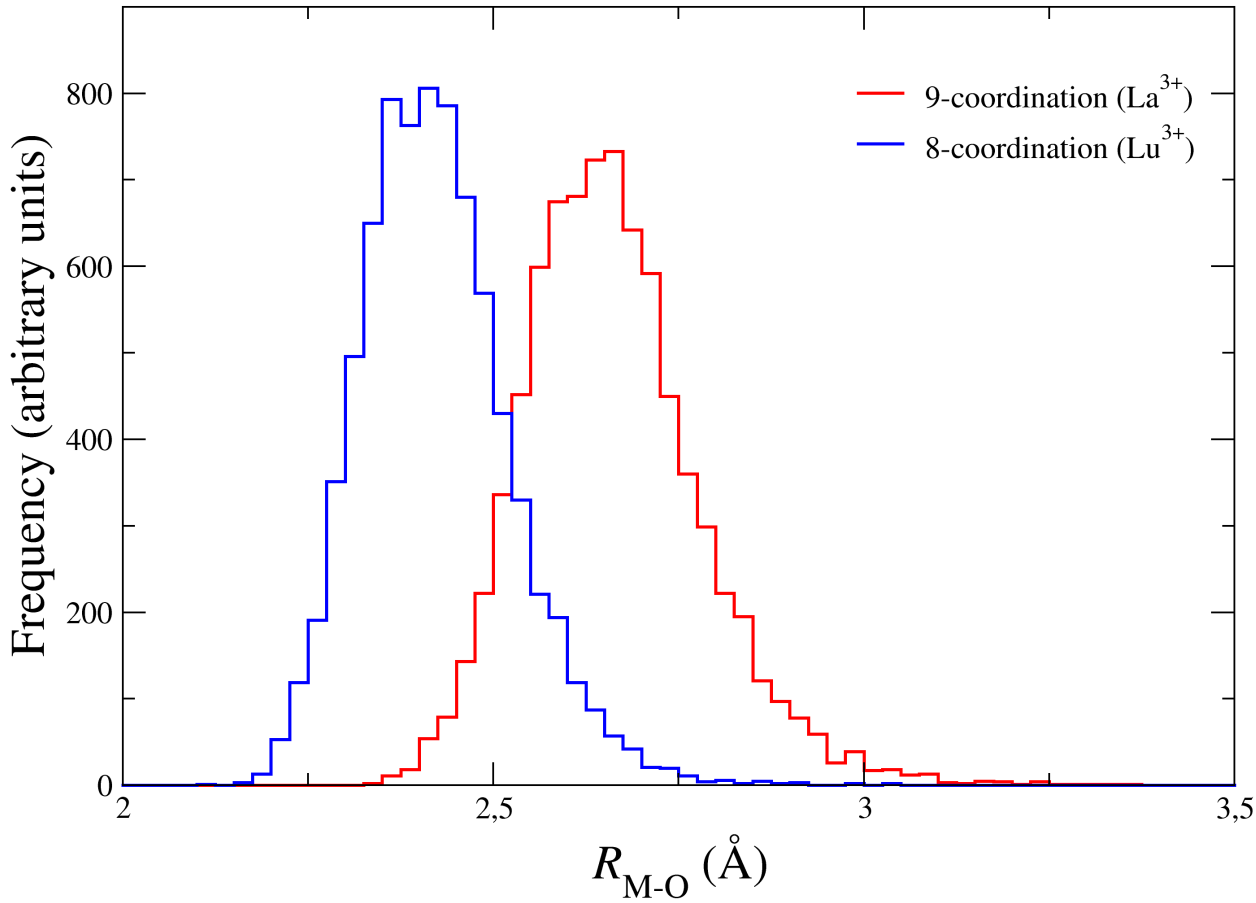


Figure S4: Histogram of M-O distances for the 8-coordinated ($Lu^{3+}$) and 9-coordinated ($La^{3+}$).